Canada

Energy, Mines and Resources Canada

Énergie, Mines et Ressources Canada

CATALYTIC HYDROGASIFICATION OF WOOD

RENEWABLE ENERGY BRANCH

PREPARED FOR:

Bioenergy Development Program
Renewable Energy Branch
Energy, Mines and Resources Canada
Ottawa, Canada
DSS Contract File No: 24ST-23216-4-6365

March 1986

PREPARED BY:

Dr. Donald S. Scott
Department of Chemical Engineering
University of Waterloo
Waterloo, Ontario N2L 3G1
(519) 885-1211 Ext. 2914

SCIENTIFIC AUTHORITY:

Dr. David P.C. Fung
Department of Energy, Mines and Resources
CANMET, ERL
c/o 555 Booth Street
Ottawa, Canada K1A 0E4

© Minister of Supply and Services Canada 1987

Catalogue No. M91-7/5-1987E
ISBN 0-662-15615-3

ACKNOWLEDGEMENTS

The principal investigator expresses his thanks to the Renewable Energy Branch of Energy, Mines and Resources Canada for the financial support which made this work possible. Dr. David Fung of CANMET also gave valuable assistance to this project in his role as Scientific Authority.

The experimental work described in this report was carried out by Mahesh Garg as a part of his MASc program, while supervision of the work was by Jan Piskorz and Dr. Desmond Radlein. The success of the investigations was due to their combined efforts, and the principal investigator is aware of his indebtedness to them for their contributions.

CITATION

Scott, D.S., M. Garg, J. Piskorz and D. Radlein, Department of Chemical Engineering, University of Waterloo. Catalytic Hydrogasification of Wood. Final Report of Contract File #24 ST.23216-4-6365. Renewable Energy Branch; Energy, Mines and Resources Canada, Ottawa, Ontario. 1986. (179 pp)

Copies of this report may be obtained through:

Renewable Energy Branch
Energy, Mines and Resources Canada
580 Booth Street
Ottawa, Ontario
K1A 0E4

OR

CISTI Library
National Research Council
Bldg. M-55, Montreal Road
Ottawa, Ontario
K1A 0S2

DISCLAIMERS

This report is distributed for informational purposes only and does not necessarily reflect the views of the Government of Canada nor constitute an endorsement of any commercial product or person. Neither Canada nor its ministers, officers, employees or agents makes any warranty in respect of this report or assumes any liability arising out of this report.

PREFACE

This report is an account of an investigation to establish the potential of a novel concept in biomass gasification. It covers work done over a twelve-month period in 1985 in the Pyrolysis Laboratory of the Department of Chemical Engineering, University of Waterloo, under the direction of Dr. Donald S. Scott, Principal Investigator.

At the initiation of the study, only a few key experiments had been done that opened up the possibility of a somewhat different approach to biomass gasification. The present work was intended to investigate in more detail the variables of the process, and to gain some insight into the controlling phenomena. While these objectives were successfully accomplished, much remains to be done to establish the commercial potential of this new gasification method.

Several well developed technologies exist for biomass gasification, at least at the pilot plant or demonstration plant scale. The most promising of these for syngas manufacture are probably the steam-oxygen or steam pyrolysis processes, either catalytic or non-catalytic. However, the process investigated in this work gasifies wood over a catalyst in a hydrogen atmosphere at atmospheric pressure and relatively low temperatures to produce a methane-rich gas which can be reformed to yield a synthesis gas.

The process is probably most suitable for smaller scale gasification and would be of interest for the generation of high heating value gas or of synthesis gas in remote locations, inasmuch as the only process inputs are wood, a little water and process energy. However, present investigations have studied only the nature of the gasification reactor so far. The integrated process has not yet been operated, although this could be readily done on a laboratory scale inasmuch as other required process units employ conventional technology.

ABSTRACT

The operation of a novel atmospheric pressure fluidized bed catalytic hydrogasification process developed in our laboratory was investigated for poplar wood. At nearly optimal conditions, a specially prepared nickel-on-alumina catalyst gave 70% to 75% carbon conversion to methane, with a gas selectivity of 95%. Product gas containing a high percentage of methane could be obtained because of the low temperatures of operation. Optimal gasifier conditions with respect to residence time, temperature, feed-to-catalyst ratio, and catalyst composition and type were established. A concept for an integrated small-scale (100 t/day) syngas production unit is proposed which would yield a product gas with H_2/CO ratio of one. Wide flexibility can be achieved by the addition of a shift reactor. The proposed gasification process could be readily pressurized, it would produce an undiluted gas and would require no input except wood and some water, both of which are consumed. All process units required, except the hydrogasifier, are conventional technology. Preliminary estimates suggest that the cost of methane production, if wood or woody biomass is the feed, may be lower from this process than from other alternatives also using wood feed.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
PREFACE	iv
ABSTRACT	vi
EXECUTIVE SUMMARY	x
RÉSUMÉ	xix
1. INTRODUCTION	1
2. OBJECTIVES	5
3. METHODS	7
3.1 Apparatus	7
3.2 Experimental Procedure	14
3.2.1 Set-up	14
3.2.2 Reduction of Catalyst	14
3.2.3 Experimental Run	15
3.2.4 Shutdown Procedure	16
3.3 Analysis of Products	17
3.3.1 Gases	17
3.3.2 Liquids	17
3.3.3 Chars	19
3.4 Catalyst Preparation	21
3.5 Feed Used	22
3.6 Sources of Error	24

4. RESULTS AND DISCUSSION 26

4.1 Introduction 26

4.2 Preliminary Experiments 28

4.3 Effect of Nickel Content 39

4.4 Effect of Hydrogen Atmosphere 44

4.5 Effect of Temperature 46

4.6 Effect of Residence Time 55

4.7 Effect of Feed/Catalyst Ratio 56

4.8 Effect of Alumina Support 67

4.9 Comparison of Hydrogasification with Different Solids 70

4.10 Effect of Catalyst Regeneration 72

4.11 Hydrogasification of Cellulose 74

4.12 Hydrogasification of Char 77

4.13 Hydrogasification with Ru Catalyst 79

4.14 Hydrogasification with Co-Mo Catalyst 82

4.15 Gasification with a $CO+H_2$ Mixture 84

4.16 Gasification with a CO_2+H_2 Mixture 88

4.17 Tests of Miscellaneous Commercial Catalysts 91

4.18 Preliminary Tests of Catalyst Lifetimes 96

5. EQUILIBRIUM CALCULATIONS 104

5.1 Method 104

5.2 Effect of Temperature 105

5.3 Effect of F/C Ratio 114

5.4 Effect of Hydrogen-to-Feed Ratio 121

6. SUMMARY AND DISCUSSION OF MECHANISMS 131

6.1 Discussion of Product Yields 131

6.2 Mechanism of Carbon Deposition on the Catalyst 143

7. CONCLUSIONS 149

8. RECOMMENDATIONS 158

REFERENCES 161

TABLES 163

ILLUSTRATIONS 165

APPENDICES 167

Appendix A 167

Appendix B 169

Appendix C 179

EXECUTIVE SUMMARY

Previous work had shown that wood could be catalytically methanated at temperatures from 400°C-600°C at one atmosphere of hydrogen pressure. High yields of methane were obtained in the few experiments conducted. The principal objective of the present study was to verify these results, and to investigate the variables affecting the yield of methane and other products during the low-pressure low-temperature catalytic hydrogasification of poplar wood. From the results, a concept for an integrated gasification system was to be developed based on steam reforming of the methane to yield a synthesis gas, and the recycling of some product gas to yield the necessary hydrogen stream. The overall gasification process can be represented by the idealized stoichiometric equation

$$2\ \underset{\text{(wood)}}{C_6H_9O_4} + 4\ H_2O \longrightarrow 12\ CO + 13\ H_2$$

This equation is actually the sum of three separate process steps represented by the relations below:

Hydrogasification $\quad 2\ C_6H_9O_4 + 23\ H_2 \longrightarrow 12\ CH_4 + 8\ H_2O$

Steam Reforming $\quad 12\ CH_4 + 12\ H_2O \longrightarrow 12\ CO + 36\ H_2$

Diffusional Separation $\quad 12\ CO + 36\ H_2 \begin{cases} \nearrow 36\ H_2 \longrightarrow 23\ H_2 \\ \searrow 12\ CO \rightarrow 12\ CO + 13\ H_2 \end{cases}$

The present work was confined to a study of the first stage, that is, the unique hydrogasification process developed in our earlier work. The steam reforming and diffusional separation steps represent known technology.

The investigation was carried out in the bench scale atmospheric pressure fluidized bed reactor system developed in our laboratories for studies of biomass pyrolysis. This apparatus has been described in several articles by Scott and Piskorz (1982, 1984). As employed for this work, a stainless steel fluidized bed reactor was used holding about 50 g of catalyst and operating with a continuous feed of -250 +120 µm poplar sawdust of about 50 g per hour. Product gases, tar and char yields were measured as a function of process conditions. Results were quite reproducible for this kind of small-scale continuous operation. However, the apparatus and methodology of the bench scale pyrolysis unit have been thoroughly tested and evaluated in our laboratories in the course of several years of development and use, so that experimental problems were minimal.

Results were obtained for investigations of the following variables: temperature, residence time, feed-to-catalyst ratio, amount of metal in the catalyst, type of catalyst and effect of catalyst regeneration. In addition, some tests were also done as an aid in proposing a possible mechanism

for the gasification reaction. The influence of the different variables is briefly summarized below.

Bed Material - CH_4 yield was very low with sand as the bed solids but tar yield was 55% to 65% of wood feed. With the γ-alumina support alone, gas yield was much larger, and tar yield was greatly reduced. When a nickel-on-alumina catalyst was used, 70% to 75% carbon conversion to CH_4 could be obtained with a gas selectivity of 95% and a tar yield of only 1% to 2% of the wood feed.

Catalyst Nickel Content - A series of nickel-on-alumina catalysts prepared in our own laboratories was used. While yields of CH_4 + CO increased with increasing Ni content over the range of 3% to 50%, above about 8% Ni content the increased yield was marginal. It was concluded that any Ni content above 8% would give satisfactory performance.

Catalyst Type - Some commercial nickel-on-alumina catalysts performed as well as those prepared in-house, but impurities in them, especially carbon additive, made it difficult to use them for precise work. Ruthenium and cobalt-molybdenum catalysts were inferior to nickel catalysts, at least for the production of methane.

Temperature - A maximum yield of CH_4 per kg of wood feed was obtained at temperatures around 550°C. Maximum selectivity for CH_4 occurred at 500°C where the gas composition (vol. %) was 95.7% CH_4, 2.7% CO and 1.5% CO_2 (H_2-free basis). At this temperature, CH_4 yield was 97.5% of the maximum obtained at 550°C. At high temperature (650°C), methane content and yield decreased, although total gas production (moles/kg wood) increased, as well as the total yield of reformable gas (CO + CH_4 + hydrocarbons), with large increases in CO yield. It was shown that this change in CH_4/CO ratio was an equilibrium effect, and gas phase equilibrium was most closely approached at 650°C. Char yield at all temperatures was very similar to that found for noncatalytic thermal pyrolysis of wood.

Feed/Catalyst (F/C) Ratio - A feed/catalyst weight ratio greater than 2.0 h^{-1} resulted in increased tar and char yields with corresponding reduction in the methanation process. It was concluded that an F/C ratio of about 1.5 would be suitable. In fact, this feed/bed solids ratio is essentially the same as that used for the Waterloo Fast Pyrolysis process for the thermal pyrolysis of biomass.

Residence Time - Gas residence time can be varied only over narrow limits in a small diameter fluidized bed. However, within this limitation it appeared that an apparent gas residence time (net empty reactor volume/volumetric gas flow rate at reactor inlet conditions) of 0.44 seconds or less would be most appropriate. Accordingly, nearly all tests were done at close to 0.44 s residence time.

Catalyst Regeneration - Regeneration of catalyst by burning off accumulated carbon deposits and re-reducing did not appear to cause any noticeable loss in catalyst activity over three cycles.

Carbon Deposition - Carbon deposition on the catalyst increased significantly with the F/C ratio as this ratio was increased from 0.74 to 3.68. At an F/C ratio of about 1.5, the carbon deposition rate increased only slightly as temperature varied from 400°C to 650°C with values being from 3% to 4.5% of the catalyst weight. This amount of carbon did not appear to inhibit catalyst activity to any great extent. However, at high F/C ratio when greater amounts of carbon were formed, some detrimental effect on activity probably resulted.

Evidence was found that the presence of some CO_2 in the hydrogen feed gas would reduce the amount of secondary

carbon deposition on the catalyst surface. The bulk of char formed in the hydrogasification reaction is primary carbon and is not formed on the catalyst surface, but results from the initial pyrolytic decomposition of the wood.

From the results of the experimental program, a possible mechanism for the hydrogasification reaction can be proposed. The first stage is a thermal pyrolysis, essentially the same as that which occurs in the Waterloo Fast Pyrolysis process for biomass, inasmuch as all reaction conditions are the same except for the presence of a catalyst and a hydrogen atmosphere. The organic volatiles generated adsorb on the catalyst surface where cracking occurs to yield CO, H_2O and small organic molecules. The CO and small organic molecules react readily with adsorbed H_2 on the nickel surface to form CH_4. It is felt that most of the CO_2 is either a primary product of thermal pyrolysis, or is produced as a secondary product from gas phase reactions. Much of the water yield obtained parallels the CH_4 yield, indicating that the methanation reaction involves adsorbed CO or carbonyl groups. Conversion to CH_4 decreases if the feed/catalyst ratio is too high, so that too much tar is formed for the available cracking and hydrogenation rate. High carbon deposition at high F/C ratios also reduces the catalyst effectiveness. At high temperatures catalyst

selectivity for CH_4 appears to decrease, but this is primarily because of equilibrium considerations. At 650°C, gas phase equilibrium is closely approached.

The proposed gasification process appears to be well suited to small-scale operation and for pressure operation. Higher hydrogen pressures would improve gasifier performance, and probably catalyst lifetime. The process generates a clean syngas with a H_2/CO ratio of about one. However, by use of the shift reaction, this can be adjusted to higher H_2/CO ratios. The process can be operated with a shift reactor added to allow simultaneous production of both a high CH_4 content gas (90% or more) and a syngas with any desired H_2/CO ratio. The process uses no raw material except wood and some water. All water added is consumed and any tar is cracked in the steam reformer, so that no waste streams are produced (except possibly some CO_2 and ash) and the process is environmentally benign. Except for the hydrogasifier itself, all other required process units are established technology. Compared with normal air or oxygen gasifiers, the proposed process produces an undiluted gas, and a minimum of CO_2. Compared with steam gasification, catalytic or noncatalytic, our process operates at much lower temperature in the gasifier with a low steam partial pressure so that the equilibrium is favorable for high CH_4 yield and selectivity. The flexibility of first producing a CH_4-rich gas

and then steam reforming it allows a spectrum of gas compositions to be produced for any particular purpose. Compared with biogas production by fermentation from wood or other organic matter, our process produces nearly twice as much CH_4 per kg of organic matter as does a biogas process, and has no effluent problems.

Preliminary conservative order-of-magnitude cost estimates suggest that the conservative cost of methane production from wood, with green wood feed at $40/BDT in a 100 dry tonne/day plant would be about 20¢ to 25¢/m^3, or $6 to $7/1000 cubic feet. These costs allow a 30% return on investment. Capital costs would be low for an atmospheric pressure process. While these figures are early estimates (±30%), and are for a small-scale plant, they indicate considerable commercial potential, especially for areas where natural gas or fossil fuels are not readily available. Also, the costs given above are quite sensitive to the original cost of the biomass used.

Further work is required to fully evaluate one or more commercial catalysts for the gasification process, and to study the effect of pressure operation. A small-scale integrated complete unit (100 g per hour of wood feed) would be practical for gathering data on operation of the process as a complete system, and for supplying the necessary data for a mathematical model.

The proposed process is unique in its concept and technology, and offers potential advantages, especially for smaller scale pressure operation, which make further development worthwhile. The results of the present study demonstrate successful operation of the hydrogasifier at atmospheric pressure. Investigation of hydrogasification on a larger scale (2 kg/h) would also be warranted, in addition to tests on a pressurized bench scale unit. All of this work could be carried out in our laboratories with minimal capital cost, inasmuch as the 2 kg/h gasifier reactor already exists.

RÉSUMÉ

Des travaux antérieurs ont montré que l'on pouvait, par des méthodes catalytiques, transformer le bois en méthane, à des températures comprises entre 400 °C et 600 °C, sous une pression d'hydrogène d'une atmosphère. On a obtenu une production élevée de méthane lors des quelques expériences réalisées. Dans la présente étude, notre objectif prinipal était la vérification de ces résultats, et l'étude des variables influant sur la production de méthane et d'autres produits durant l'hydrogazéification catalytique du bois de peuplier à basse pression et à basse température. D'après les résultats, on devait établir le principe d'un système intégré de gazéification basé sur le reformage à la vapeur du méthane pour obtenir un gaz de synthèse, et le recyclage de certains produits gazeux pour obtenir l'afflux nécessaire d'hydrogène. On peut représenter le processus global de gazéification dans l'équation stoechiométrique idéalisée:

$$2\ \underset{\text{(bois)}}{C_6H_9O_4} + 4\ H_2O \longrightarrow 12\ CO + 13\ H_2$$

Cette équation est en fait la somme de trois étapes distinctes du procédé, représentées par les relations ci-dessous:

Hydrogazéification $2\ C_6H_9O_4 + 23\ H_2 \longrightarrow 12\ CH_4 + 8\ H_2O$

Reformage à la vapeur $12\ CH_4 + 12\ H_2O \longrightarrow 12\ CO + 36\ H_2$

Séparation par diffusion $12\ CO + 36\ H_2 \longrightarrow 36\ H_2 \longrightarrow 23\ H_2$

$12\ CO \longrightarrow 12\ CO + 13\ H_2$

Ce travail s'est limité à une étude de la première étape, soit l'unique réaction d'hydrogazéification que nous ayons mise au point lors de nos travaux de recherche antérieurs. Les étapes de reformage à la vapeur et de séparation par diffusion représentent une technologie bien connue.

On a effectué des recherches dans un système de réacteur à lit fluidisé, de type expérimental, fonctionnant à la pression atmosphérique. Nous avons mis au point ce système dans nos laboratoires pour étudier la pyrolyse de la biomasse. Scott et Piskorz (1982, 1984) ont décrit cet appareil dans plusieurs articles. Nous avions employé un réacteur à lit fluidisé, en acier inoxydable, contenant environ 50 g de catalyseur et fonctionnant avec une alimentation continue de -250 +120 µm de sciure de bois de peuplier, au taux d'environ 50 g par heure. On a mesuré en fonction des conditions de déroulement du procédé le rendement en gaz, goudron et produits de carbonisation. Les résultats obtenus par cette opération continue à petite échelle, se sont avérés tout à fait reproductibles. Toutefois, au cours de plusieurs années de développement et d'exploitation, nous avons testé et évalué de façon

approfondie dans nos laboratoires, l'appareillage et le monde d'emploi caractérisant l'unité de pyrolyse à l'échelle du laboratoire, de sorte que nous n'avons pratiquement pas en de problèmes expérimentaux.

On a obtenu des résultats en effectuant l'étude des diverses variables suivantes; température, temps de séjour, rapport charge/catalyseur, teneur du catalyseur en métal, type de catalyseur et effet de la régénération de ce dernier. En outre, on a aussi effectué quelques essais qui nous aideront à proposer un mécanisme possible du processus de gazéification. On donne ci-dessous un bref résumé de l'influence des diverses variables.

Matériau du lit - Avec l'emploi de sable comme matériau solide du lit, on a obtenu un rendement très faible en CH_4, mais le rendement en goudron représentait 55 % à 65 % de la charge de bois. En employant l'alumine seule, on a obtenu un rendement en gaz beaucoup plus élevé, et la production de goudron a été grandement réduite. Avec l'emploi d'un catalyseur de type nickel sur alumine, on a obtenu un taux de conversion du carbone en CH_4 de 70 % à 75 %, avec une sélectivité gazeuse de 95 % et un rendement en goudron ne représentant que de 1 % à 2 % de la charge ligneuse.

Teneur en nickel du catalyseur - Nous avons employé une série de catalyseurs de type nickel sur alumine que nous avons préparés dans nos propres laboratoires. Tandis que la production de CH_4 + CO augmentait en même temps que la teneur en Ni dans la gamme de 3 % à 50 %, on a noté qu'au-dessus d'environ 8 % de Ni, l'augmentation de rendement était marginale. On en a conclu que toute teneur en Ni supérieure à 8 % donnerait des résultats satisfaisants.

Type de catalyseur - On a obtenu des résultats tout aussi bons avec certains catalyseurs commerciaux de type nickel sur alumine, qu'avec ceux préparés dans nos propres installations, mais les impuretés qu'ils contenaient, surtout un additif à base de carbone, permettaient difficilement de les utiliser pour réaliser des travaux précis. Les catalyseurs au ruthénium et au cobalt et molybdène étaient inférieurs aux catalyseurs au nickel, du moins pour la production du méthane.

Température - On a obtenu un rendement maximum en CH_4 par kilo de charge ligneuse, aux températures se situant autour de 550 °C. On a observé une sélectivité maximum vis-à-vis du CH_4 à 500 °C, lorsque la composition du gaz (pourcentage volumétrique) était de 95,7 % de CH_4, 2,7 % de CO et 1,5 % de CO_2 (en

l'absence de H_2). À cette température, la production de CH_4 représentait 97,5 % du maximum obtenu à 550 °C. À température élevée (650 °C) la teneur et le rendement en méthane ont diminué, bien que la production totale de gaz (moles/kg de bois) ait augmenté, de même que le rendement total en gaz reformable (CO + CH_4 + hydrocarbures), et que le rendement en CO ait montré une augmentation importante. On a démontré que cette variation du rapport CH_4/CO représentait un effet d'équilibre, et que l'on se rapprochait le plus de l'équilibre des phases gazeuses à 650 °C. À toutes les températures, le rendement en produits de carbonisation se rapprochait étroitement de celui observé lors de la pyrolyse non catalytique du bois.

Rapport charge/catalyseur (F/C) - Un rapport pondéral charge/catalyseur supérieur à 2 a permis d'augmenter le rendement en goudron et produits de carbonisation, et de les réduire d'autant lors du processus de méthanisation. On en a conclu qu'un rapport F/C d'environ 1,5 conviendrait. En fait, ce rapport charge/solides du lit est essentiellement le même que celui que l'on emploie lorsqu'on applique le procédé Waterloo de pyrolyse rapide à la pyrolyse thermique de la biomasse.

Temps de séjour - On ne peut faire varier le temps de séjour des gaz que dans d'étroites limites, à l'intérieur d'un lit fluidisé de petit diamètre. Toutefois, on a constaté que dans ces limites, un temps de séjour apparent du gaz (volume net du réacteur vide/débit de gaz, dans les conditions à l'admission dans le réacteur) de 0,44 seconde ou moins conviendrait le mieux. En conséquence, on a effectué presque tous les essais avec un temps de séjour proche de 0,44 s.

Régénération du catalyseur - Il ne semble pas que la régénération du catalyseur par combustion des résidus de carbone accumulés et par une nouvelle étape de réduction ait produit une perte décelable d'activité du catalyseur durant trois cycles.

Dépôt du carbone - Le dépôt de carbone sur le catalyseur a nettement augmenté en même temps que le rapport F/C, lorsqu'on a accru ce rapport de 0,74 à 3,68. Avec un rapport F/C d'environ 1,5, le taux de dépôt du carbone n'a que légèrement augmenté alors que la température variait de 400 °C a 650 °C; les taux se situaient entre 3 % et 4,5 % du poids de catalyseur. Il ne semble pas que cette quantité de carbone ait inhibé l'activité du catalyseur dans une mesure importante. Toutefois, lorsque le rapport F/C était élevé, et que des quantités plus grandes de carbone se

formaient, il y a probablement eu un effet inhibiteur de l'activité.

On a constaté que la présence d'une petite quantité de CO_2 dans le gaz d'alimentation à base d'hydrogène, avait pour effet de réduire le taux de dépôt secondaire de carbone à la surface du catalyseur. La totalité du produit de carbonisation que donne la réaction d'hydrogazéification est du carbone primaire, et ne se forme pas à la surface du catalyseur, mais résulte de la décomposition pyrolytique initiale du bois.

D'après les résultats du programme expérimental, on peut proposer un mécanisme possible de la réaction d'hydrogazéification. La première étape est une pyrolyse thermique, essentiellement identique à celle du procédé Waterloo de pyrolyse rapide de la biomasse, dans la mesure où toutes les conditions de réaction sont les mêmes, excepté la présence d'un catalyseur et d'une atmosphère d'hydrogène. Les produits organiques volatiles générés sone adsorbés à la surface du catalyseur, sur laquelle a lieu le craquage qui donne CO, H_2O et de petites molécules organiques. Le CO et les petites molécules organiques réagissent spontanément avec le H_2 adsorbé à la surface du nickel en donnant du CH_4. On estime que la majeure partie du CO_2 est soit un produit primaire de la pyrolyse, soit un produit secondaire

résultant des réactions en phase gazeuse. Une grande partie de la quantité d'eau obtenue est équivalente au rendement en CH_4, ce qui indique que la réaction de méthanisation passe par l'adsorption de CO ou de groupes carbonyles. La conversion en CH_4 diminue si le rapport charge/catalyseur est trop élevé, de sorte qu'il se forme trop de goudron pour les taux de craquage et d'hydrogénation possibles. Un taux élevé de dépôt du carbone, lorsque les rapports F/C sont élevés, réduit aussi l'efficacité du catalyseur. Aux températures élevées, il semble que la sélectivité du catalyseur vis-à-vis du CH_4 diminue, mais ceci résulte principalement des réactions d'équilibre. À 650 °C, on se rapproche étroitement de l'équilibre des phases gazeuses.

Le procédé de gazéification proposé paraît bien adapté aux méthodes industrielles à petite échelle et aux méthodes de traitement sous pression. En élevant la pression d'hydrogène, on augmente le rendement du gazéificateur, et probablement la longévité du catalyseur. Ce procédé permet d'obtenir un gaz synthétique épuré caractérisé par un rapport H_2/CO d'environ 1. Toutefois, en utilisant les réactions suractivées, on peut adapter le procédé à des rapports H_2/CO plus élevés. On peut proceder à la réaction en employant un réacteur catalytique, pour obtenir à la fois un gaz riche en CH_4 (90 % ou plus) et un gaz synthétique, quel que soit le rapport H_2/CO désiré. Dans ce procédé, on

n'utilise pas de matières premières, excepté du bois et un peu d'eau. Toute l'eau ajoutée est consommée, et tout le goudron présent est soumis à un craquage dans le reformeur en présence de vapeur, de sorte qu'il n'y a pas production de résidus (excepté peut-être un peu de CO_2 et de cendres) et que le procédé est peu néfaste pour l'environnement. Excepté l'hydrogazéificateur lui-même, toutes les autres installations requises représentent une technologie bien acceptée. Par rapport aux gazéificateurs normaux à air ou à oxygène, le type d'appareil proposé produit un gaz non dilué, et un minimum de CO_2. Par rapport à la gazéification catalytique ou non catalytique en présence de vapeur, le procédé que nous employons s'effectue à des températures beaucoup plus basses dans le gazéificateur, en présence d'une faible pression partielle de vapeur, de sorte que l'équilibre est favorable à un rendement élevé en CH_4 et à une bonne sélectivité. La possibilité de produire tout d'abord un gaz riche en CH_4, puis de le reformer à la vapeur, nous permet de produire, en vue d'un objectif précis, une gamme de compositions gazeuses. Comparativement à la production de biogaz par fermentation du bois ou d'autres matières organiques, notre procédé donne presque deux fois plus de CH_4 par kg de matière organique que la méthode de production de biogaz, et ne pose pas de problèmes de rejet d'effluents.

Des estimations préliminaires prudentes relatives à l'ordre de grandeur des dépenses nous suggèrent que le coût de la production de méthane à partir du bois, l'alimentation étant constituée de bois vert à 40 $ la tonne sèche, dans une usine traitant 100 tonnes de bois sec par jour s'élèverait à environ 20 ¢ à 25 ¢ par m^3, soit à 6 $ à 7 $ par 1000 pi^2. Cette somme permet un rendement de 30 % du capital d'investissement. Les frais de premier établissement seraient faibles dans le cas d'un procédé s'effectuant à la pression atmosphérique. Ces chiffres représentent une estimation préliminaire (± 30 %) et s'appliquent à une usine de petite échelle, mais indiquent des possibilités commerciales considérables, surtout dans les secteurs où l'on ne peut facilement s'approvisionner en gaz naturel ou en combustibles fossiles. De plus, les coûts cités plus haut sont assez nettement sensibles au coût initial de la biomasse utilisée.

Il est nécessaire de poursuivre les recherches pour pleinement évaluer l'utilisation d'un ou de plusieurs catalyseurs du commerce dans le procédé de gazéification, et pour étudier l'effet de la réaction sous pression. Il serait pratique de disposer d'une installation complète intégrée de petites dimensions (charge de bois de 100 g par heure), pour recueillir des données sur le fonctionnement du procédé en tant que système complet et fournir les données

nécessaires à l'établissement d'un modèle mathématique.

Le procédé que l'on propose est unique du point de vue de sa conception et de sa technologie, et offre des avantages potentiels, surtout dans les installations à petite échelle fonctionnant sous pression; d'autres travaux de perfectionnement se justifieraient donc. Les résultats de la présente étude démontrent le bon fonctionnement de l'hydrogazéificateur à la pression atmosphérique. Des études de l'hydrogazéification à plus grande échelle (2 kg/h) se justifieraient, outre les essais conduits sur une installation pressurisée à l'échelle du laboratoire. Tous ces travaux de recherche pourraient être réalisés dans nos laboratoires avec des frais minimaux de premier établissement, d'autant plus qu'il existe déjà un réacteur de gazéification d'une capacité de 2 kg/h.

CATALYTIC HYDROGASIFICATION OF WOOD

by Donald S. Scott, Mahesh Garg, Jan Piskorz and Desmond Radlein

Department of Chemical Engineering, University of Waterloo

1. INTRODUCTION

Biomass is generally not a fuel with ideal properties, and this is particularly true of waste forest biomass. As a fuel, it is bulky and of low density, it is costly to transport, and it does not store well. It has a low heating value unless well dried. In addition, the supply of raw material, particularly wastes which can be obtained at a given site, is usually limited by the harvesting and transportation costs.

The need to find new sources of liquid fuels, especially from renewable resources, has led to worldwide development of research on methods of converting synthesis gas ($CO + H_2$) to liquid hydrocarbons suitable for use as motor fuels. Two processes on which intensive investigations have been carried out are the Fischer-Tropsch synthesis and the Mobil methanol-to-gasoline conversion process. Both of these processes could be operated fairly efficiently in small-scale units if a supply of clean, inexpensive synthesis gas were available. Biomass is an ideal source of syngas for these catalytic processes, inasmuch as it has a very low sulfur content, and a relatively low nitrogen content.

Hence, the possibility exists of producing liquid fuels, particularly methanol, from waste biomass if efficient small-scale gasification units could be developed. If these gasification units could be operated in remoter locations, this would be an added advantage.

Steam-oxygen gasification is one of the more highly researched gasification processes for biomass, and it is capable of yielding a good-quality synthesis gas. The use of air would introduce large quantities of nitrogen into the syngas and is therefore less desirable. The use of oxygen (as opposed to air), however, requires an air separation plant to produce a reasonably good grade of oxygen. Such plants are relatively expensive and generally not economic on a smaller scale.

Steam gasification can also be used to produce a good-quality syngas, but high temperatures are required for the reaction and a good deal of carbon is often converted to carbon dioxide with a loss of yield of syngas. Further, control to produce the desired ratio of CO/H_2 (1:1 to 2:1 depending on the process) is often difficult to achieve in a single reactor.

Hence, one of the problems of existing syngas production methods from biomass is that auxiliary units are required, that is, oxygen plants and/or high-temperature steam

generators. These requirements make these processes best suited for larger scale operations. Frequently, the supplying of large quantities of biomass at a single manufacturing location for such a process would not be economical.

The present study is a preliminary investigation of an alternative route to biomass gasification by use of a catalytic hydrogasification method developed in our laboratories in the Department of Chemical Engineering of the University of Waterloo.

The basic concept of this approach can be summarized in the two idealized stoichiometric equations below, assuming cellulose as a model compound.

(1) $C_6H_{10}O_5 + 12\ H_2 = 6\ CH_4 + 5\ H_2O$ (Catalyst, 400°-550°C)

(2) $6\ CH_4 + 6\ H_2O = 6\ CO + 18\ H_2$ (Catalyst, 750°C)

The overall reaction occurring in the two stages is

(3) $C_6H_{10}O_5 + H_2O = 6\ CO + 6\ H_2$

In other words, cellulose is converted to its equivalent yield of CO and H_2. The first reaction is novel, and is the one discovered in our earlier work which led to the present study. The second reaction represents conventional steam reforming technology.

If whole wood is used, the overall reaction given in equation (3) might be better represented by

(4) $2\ C_6H_9O_4 + 4\ H_2O = 12\ CO + 13\ H_2$

The gas produced in this process would have a CO/H_2 ratio of about unity. However, this ratio can be readily adjusted by the use of steam addition and the shift reaction to yield any CO/H_2 ratio desired, with some loss of carbon conversion. It is also possible to produce hydrogen primarily, or to produce a very high heating value gas with a high CH_4 content by reforming by reaction (2) only a part of the product stream from the wood gasification step in order to supply the hydrogen input steam. This flexibility is one of the potentially attractive features of this proposed process. The fact that the process is operable at atmospheric pressure and at temperatures well below those normally used for gasification is also an encouraging aspect.

2. OBJECTIVES

The principal objective of the present study was to carry out a preliminary study to verify a result obtained in earlier work, that wood could be made to undergo catalytic methanation in a hydrogen atmosphere. If satisfactory methane yields were possible, then the methane-rich gas could be reformed in a conventional steam reformer to yield either a synthesis gas or a source of hydrogen. Concepts of a potential process were to be developed, particularly for smaller-scale operations, and some preliminary order-of-magnitude cost analysis carried out.

Because only one or two key experiments had been previously carried out (Scott et al., 1985), the principal objective was the development of the methanation technology, and of experimentation to give some understanding of the process. This study required not only evaluation of the effect of process parameters such as temperature, feed rate, etc., but also development of appropriate catalysts, study of different catalyst compositions and some preliminary evaluation of catalyst performance and lifetime.

From the experimental results a concept has been developed for an integrated process, which could be developed at the laboratory- scale level. Further, a comparison has been

made between the yields obtained in the experimental methanation system and those thermodynamically probable.

Of the above objectives, substantially all have been met. Only the cost analysis is incomplete, inasmuch as some costs and performance data were not available for the process units employing conventional technology.

3. METHODS

3.1 Apparatus

The arrangement of apparatus used for the hydrogasification of wood experiments is shown in Figure 3.1. This apparatus was to a large degree the same as that developed in our laboratories for bench scale studies of the Waterloo Fast Pyrolysis process (Scott and Piskorz, 1982a). Wood particles, which in this work were prepared from clean hybrid poplar wood, normally with a size range of 105-250 μm, were placed in the Scott low-rate biomass feeder. This feeder has been described elsewhere (Scott and Piskorz, 1982b) and its use allowed controlled biomass feed rates of 15 to 100 g/hour. A diagram of the feeder design is shown in Figure 3.2. Two gas streams entered into the feeder: (i) the gas flowing through the entrainment tube which pneumatically transported the wood to the pyrolysis reactor and (ii) the gas which flowed into the top of the feeder, then down through the feeder bed and out through a 1.85 mm diameter orifice into the entrainment tube with the solids.

The feed rate of biomass could be controlled by varying the proportions of these two gas flow rates and by changing the speed of the mechanical stirrer in the

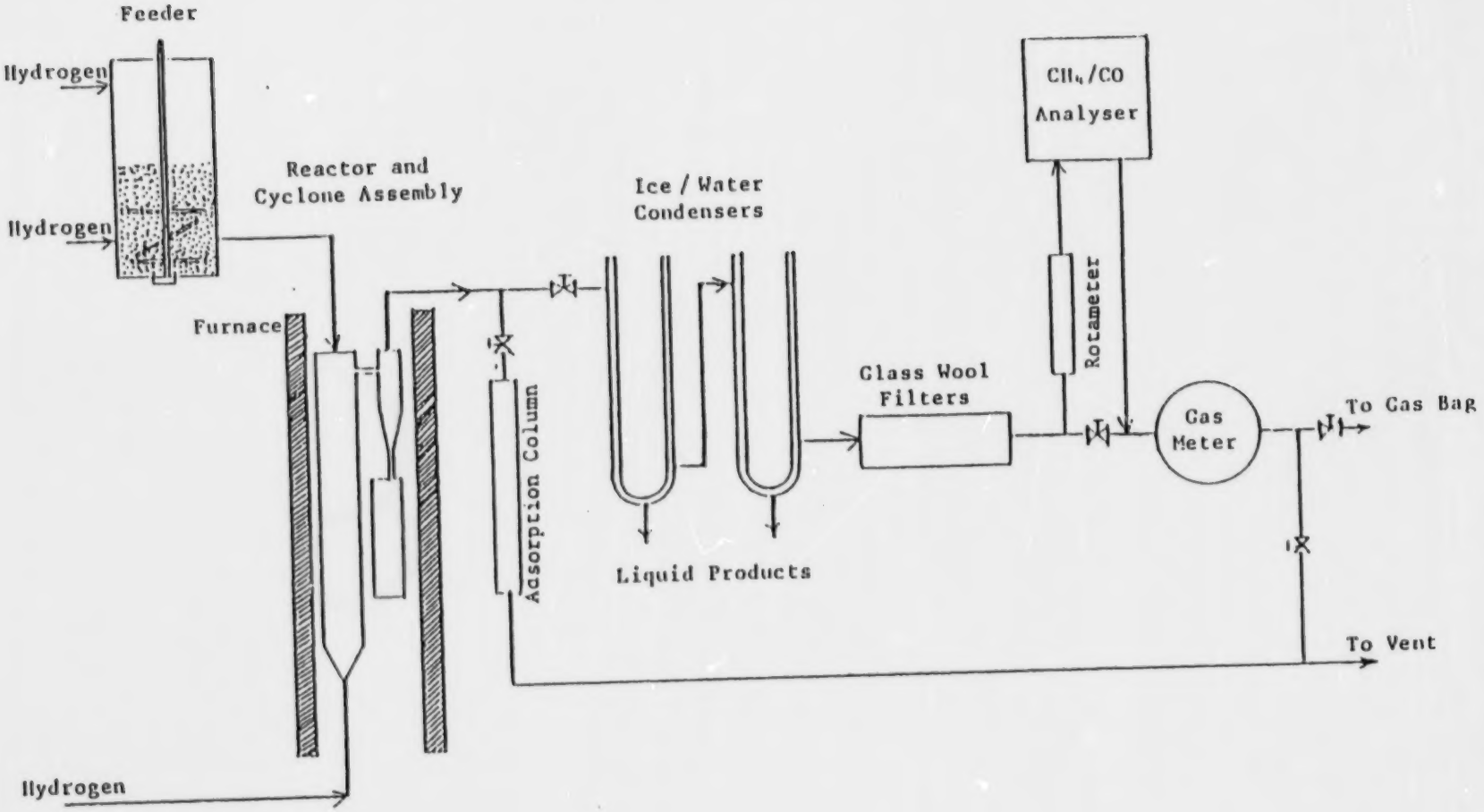


Figure 3.1 : Process Flow Diagram for Catalytic Hydrogasification of Wood

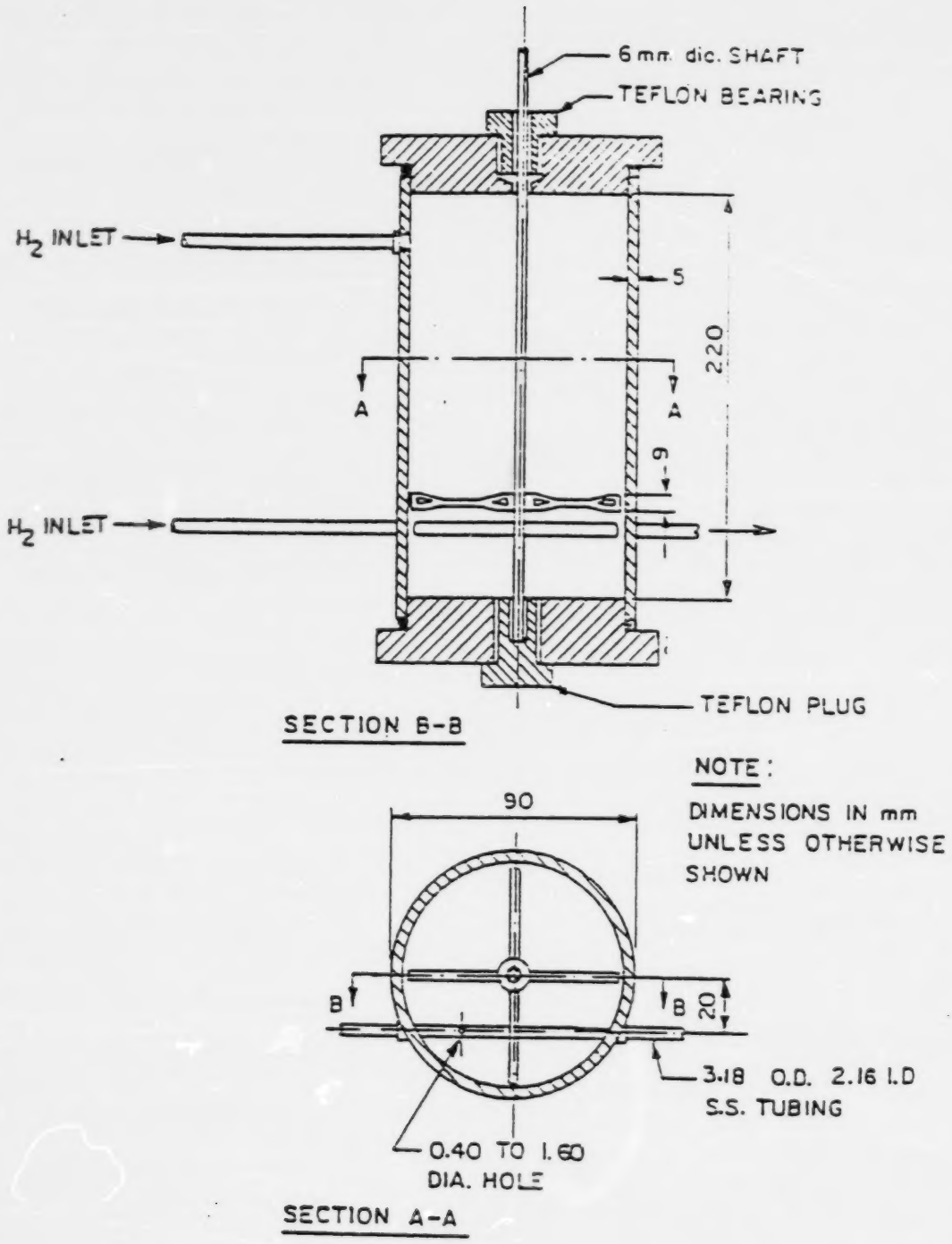


Figure 3.2 : Diagram of Solids Feeder

solids bed. Typical results of feeder tests are shown in Figure 3.3. The feed rates remained constant within 5% over periods of 90 minutes or more and could be reproduced within ±5% by controlling flowrates and stirring speeds.

Details of the pyrolysis reactor and cyclone assembly are shown in Figure 3.4. The sawdust entered into the middle of the fluidized bed of catalyst particles in the reactor. Extra fluidizing gas entered the bottom of the reactor after being preheated to the reactor temperature by a furnace. The reaction temperature of the process was measured by a thermocouple located in the middle of the fluidized bed. The gaseous and vapour products and any solid residues from the reaction exited out the top of the reactor and immediately entered a cyclone designed to remove all the solid particulate remaining in the vapours.

About 25% of the gas flow entered down the central tube of the reactor as entrainment gas carrying the wood particles. The hydrogen gas was used as the entrainment gas as well as the fluidizing gas. A part of this gas reacted with the wood in the reactor and the rest helped to carry the gasification products out of the reactor. For Runs G-3, G-4 and G-5, wood particles in the size range of 250-590 μm were used, but to ensure a

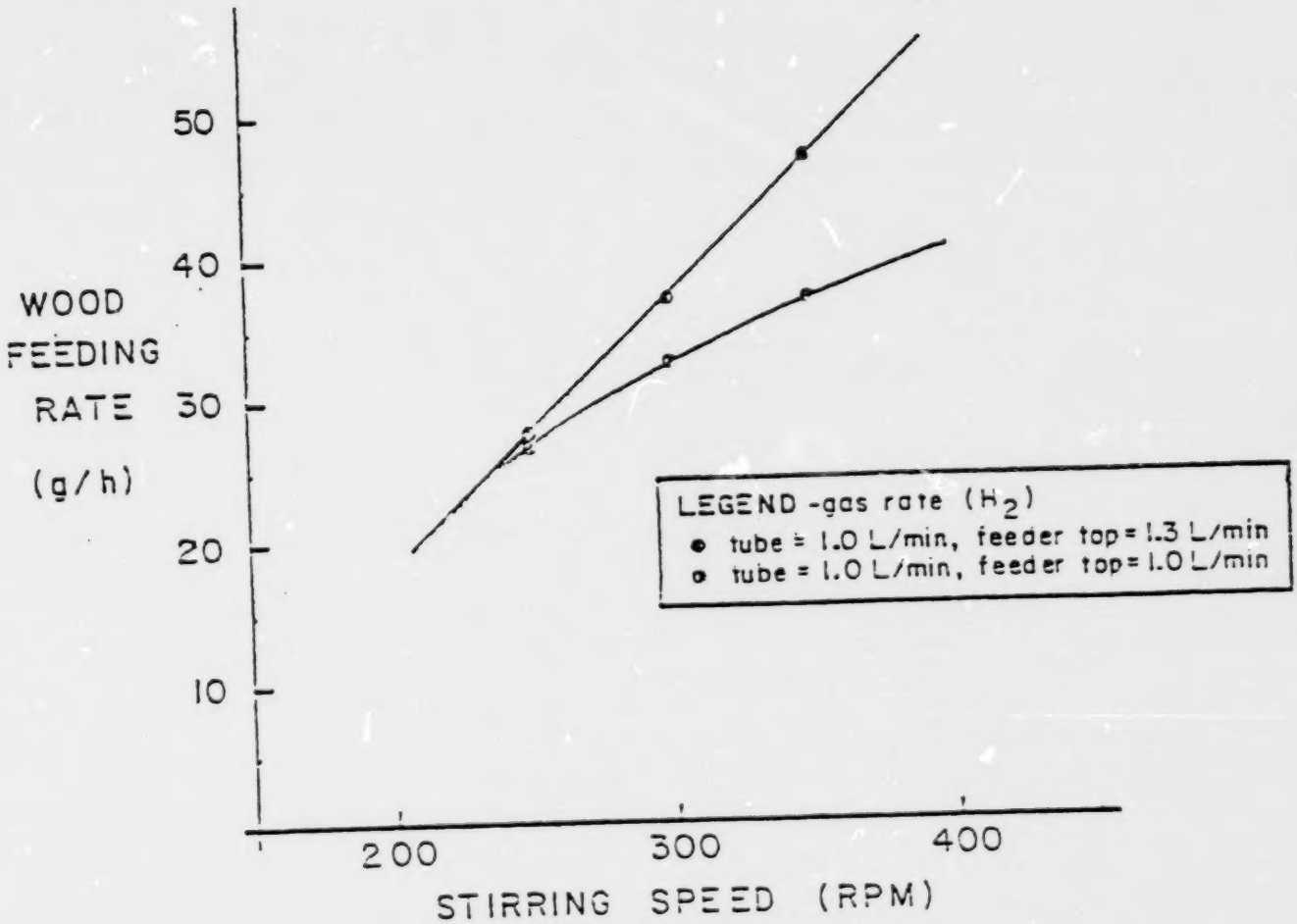


Figure 3.3 Effect of Different Gas Rates and Stirring Speeds on the Sawdust Feed Rate. Poplar Wood, 149 - 250 m

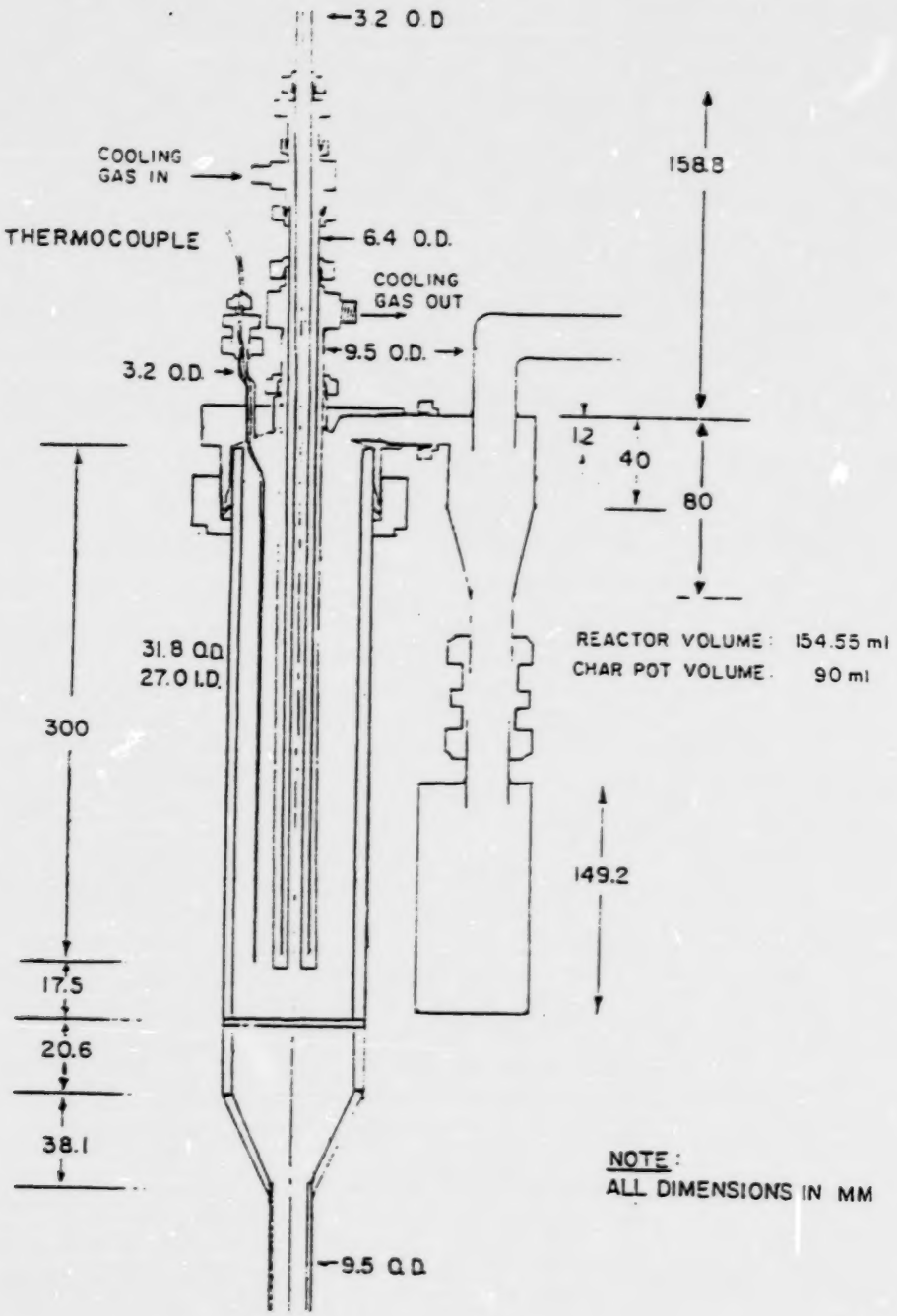


Figure 3.4 Diagram of the Catalytic Reactor and Cyclone Assembly

uniform feed rate, smaller particles between 105-250 μm were fed after Run G-5. Feed entered into the lower portion of the fluidized bed of catalyst particles, which were usually 250-590 μm in size.

The gasification products were collected in two ice-water condensers, a glass wool filter and a char pot. Char (and catalyst particles, if any,) were separated from gaseous products by the cyclone and collected in the char pot (volume of 90 mls), attached at the bottom of the cyclone. Both cyclone and char pot were heated to the reactor temperature to avoid any condensation in the cyclone. The condensable products were collected in vials, attached at the bottom of the ice-water condensers. Any entrained solid particles or liquid droplets in the gas, were collected on the glass wool filter. The outlet from the glass wool filters was joined to a main gas line. Another line was constructed from this main gas line to draw a small fraction of product gas for a continuous CH_4/CO infrared analyser (Anarad Model Ar-60). The outlet from the infra red analyser was connected back into the main gas line, which was then connected to the gas bag via the gas meter. All non-condensable gases, together with the unreacted hydrogen gas, were collected in a large polyethylene bag. The reactor, feeder and all vessels and

lines could be dismantled, weighed and/or solvent washed at the termination of a run to allow quantitative recovery of char, tar and water fractions.

3.2 Experimental Procedure

3.2.1 Set-up

The reactor was filled with approximately 50 g of catalyst particles (250-590 μm) and cyclone and char pot were attached to the reactor. The whole assembly was weighed and placed in the furnace. Heating of the furnace was started with N_2 flow through the reactor.

3.2.2 Reduction of Catalyst

The nickel catalyst was activated by the reduction of the nickel oxides present in it. The catalyst also contained some moisture which was removed by purging of nitrogen from the bottom of the reactor. Nitrogen was passed at a temperature of 400°C for a period of 20 minutes. The water coming out of the reactor during nitrogen purging and the reduction process was adsorbed on "Silica Gel" in an adsorption column. The adsorption column was weighed before and after the nitrogen purging. When nitrogen purging was

over, the flow of gas was switched from nitrogen to hydrogen to start the reduction process. Catalyst was reduced at a temperature of 550°C for a period of 60 minutes. For most runs, 90% reduction of the catalyst could be achieved. The adsorption column was removed after the reduction process. Air was passed through the adsorption column to replace hydrogen and then it was weighed.

Deactivated catalyst from an experiment was regenerated by passing air over the catalyst at a temperature of 550°C for 1 hour to remove carbon deposits and then repeating the reduction procedure with H_2 flow.

3.2.3 Experimental Run

The feeder was about half filled with poplar wood (105-250 μm), weighed and placed in position.

The reactor was stabilized at a desired reaction temperature and a measured flow of hydrogen gas was maintained through the feeder lines and through the bottom of the reactor. The run began by starting the stirrer in the feeder, which allowed the feeder gases to entrain the wood particles and transport them to the fluidized bed

reactor. To avoid gasification of wood in the reactor feeding line, this line was air cooled. To maintain a constant reactor temperature during the run (the reaction is quite exothermic), the flow of air in the feed line cooling jacket was adjusted accordingly. The temperature of the reactor was recorded several times during the run. The experiment was usually allowed to run for 30 minutes, or until the gas bag was filled.

3.2.4 Shutdown Procedure

The feeding of wood was stopped by turning off the stirrer of the feeder. The gases were allowed to circulate for a few seconds to sweep all the reaction products out of the reactor, into the gas bag. The furnaces were switched off and the gases to the feeder and to the reactor were shut off. The valve leading to the gas bag was closed, and the valve was opened to the vent in order to prevent pressure from building up in the "hot" system and to flush out hydrogen remaining in the system. The system was purged for 30 minutes with nitrogen. The reactor and the charpot were allowed to cool without artificial assistance.

3.3 Analysis of Products

The feeder, reactor, cyclone, charpot, filters and liquid collection vials were all removed and weighed.

The condenser system including the lines were all removed and cleaned, using methanol as the solvent. The methanol solution contained water, tar and char. It was filtered through a Whatman's No. 114 filter paper. The char, retained on the filter paper, was dried at a temperature of 105°C for 30 minutes and then weighed. Gases, liquid and chars were analysed according to the following procedure:

3.3.1 Gases

The gaseous product was analysed for CO, CO_2, H_2O and gaseous hydrocarbons by gas chromatography. A summary of the gas chromatographic procedure is given in Table 3.1 From the gas analysis and the known amount of the gas collected in a bag, the mass of each gaseous component produced could be calculated.

3.3.2 Liquid

One liquid product was recovered in most runs. The liquids collected in both the vials, one

TABLE 3.1

Summary of the gas chromatographic procedure used for the analysis of gaseous products

Data station : Perkin-Elmer Sigma 10B

Instrument 1 : Perkin-Elmer Sigma 4B gas chromatograph

detector	thermal conductivity
carrier gas	hydrogen
gas flow rate	25 mL/min
inlet pressure	80 kPa

Column A : Molecular Sieve 5A

compound analysed	carbon monoxide
size	6 ft X 0.125" OD (80/100 mesh)
temperature	60°C

Column B : Poropak Q

compounds analysed	carbon dioxide, water
size	8 ft X 0.125" OD (80/100 mesh)
temperature	60°C

Instrument 2 : Perkin-Elmer 3B gas chromatograph

detector	flame ionization
carrier gas	hydrogen
gas flow rate	30 mL/min
inlet pressure	500 kPa

Column B : Poropak Q

compounds analysed	methane, ethane, ethylene, propanes butanes
size	6 ft X 0.125" OD (80/100 mesh)
temperature	45°C for 4 minutes 8°C/min increase 195°C for 10 minutes

attached with each condenser, were mixed. This mixture was then analysed for water content. Typically, it contained 90% to 97% water, about 15% of this being present in the feed and the rest being water of reaction. Water contents were determined by Karl-Fischer titration using a Brickmann Model 633 automatic titrator and Hydranal reagents.

A small amount (<1.0 g) of another liquid product "tar" was obtained by washing the condensers and condenser lines with methanol, filtering and subsequently evaporating methanol. The methanol was evaporated in a rotary evaporator at a temperature of 67°C and 150 mm of Hg pressure. For most of the runs, the amount of liquid that remained after evaporation was less than that required for elemental analysis.

3.3.3 Chars

Char was collected from the char pot and from the solids recovered from the filtration of solution from the washing of condensers and condenser lines. Char from the char pot was collected after cooling because if it contacted air while hot, it burned spontaneously. Usually, the

amount of char recovered from the filter varied from 0.05 g to 0.50 g. The elemental analysis was performed using a Perkin-Elmer Model 240C analyser.

From known amounts of the gases, liquids and chars, and the composition of the gases, and the water content of the liquids, a complete material balance could be attempted. For most runs, a recovery between 90% to 100% (based on the mass of the moisture-free wood feed) was achieved.

3.4 Catalyst Preparation

Both industrial catalysts and catalysts prepared in our own laboratory were used in the present studies. The Waterloo catalysts (designated "Lab" series) were prepared according to the procedure described by Stiles (1983).

Reagents:

Alumina catalyst support (AL-1404 T 3/16", Harshaw Chemical Co.)

Nickelous nitrate 6-Hydrate, $Ni(NO_3)_2 \cdot 2.6\ H_2O$ (Baker Chemical Co.)

3.4.1 Alumina tablets were crushed and screened to get 505 g of particles in the size range of 250-590 µm.

3.4.2 A nickel nitrate solution was prepared by dissolving 410 g of nickel nitrate in 615 g of distilled water.

3.4.3 The alumina particles were coated with the nickel nitrate solution in a Boston Gear Ratiopax-I coating device. The rotating drum was maintained at a tem peature of 80°C and the nickel nitrate was dried on the alumina support.

3.4.4 Coated particles were calcined in a muffle furnace at a temperature of 400°C for a period of 3 hours in an air atmosphere.

The nickel content of the prepared catalysts was determined by gravimetric analysis, using as reagent an alcoholic solution of dimethylglyoxime (Vogel, 1961). The detailed procedure is given in the Appendix.

3.5 Feed Used

During this study IEA Poplar standard sawdust was chosen as biomass feed for the gasification process. This sawdust was prepared from clean debarked hybrid poplar wood from the Ontario Ministry of Natural Resources plantation in Brockville, Ontario. The wood was from trees seven years old, harvested in 1982, 12.34 cm diameter (BH) and designated as Populus Deltoides, Clone D-38. It was chosen as a standard test wood by the International Energy Agency for use in comparitive work in its Biomass Thermal Liquefaction Project. The elemental analysis of this sawdust was done in our analytical laboratory.

Element	% by weight (a)
Carbon	46.4
Hydrogen	6.37
Oxygen (by diff.)	46.14
Nitrogen	0.69
Ash (11)	0.40

(a) Including 4.32% moisture in the feed
Higher heating value, maf (b) 19.5 MJ/kg
(b) Taken from the report by Beckman (1983)

To achieve a relatively constant moisture content of the feed sawdust, the feedstock was purged with nitrogen in the feeder for 32 hours. Only 1.28% moisture was removed by nitrogen in this period. Another approach was tried to verify these findings. All the wood left in the feeder after experimentation was collected separately and then the moisture content of this wood was determined. It was found that the moisture in the left-over wood was 4.07% compared with the 4.32% moisture content of the fresh feed. Therefore, the approximately 150 g of unused feed in the feeder would contribute only about 0.39 g of extra water which would be carried into the reactor with the feed entrainment gas. This amount is much less than the amount of water produced during the reaction. Therefore, the free water in the entrained gas was not considered in calculation of the gasification products.

The IEA hybrid poplar wood was used in all runs in this work except one. For comparison, in one test a highly purified microcrystalline cellulose was used, Avicel PH-102. The elemental analysis of this material is given below.

Physical properties and elemental analysis of PH-102 Avicel cellulose -

Element	% by weight (a)
Carbon	42.96
Hydrogen	6.3
Oxygen (by diff.)	50.74
Nitrogen	0.0
Ash	0.0

(a) Including 2.9% moisture

Average particle size 100 μm

The procedures for using this material were identical to those used for the poplar sawdust.

3.6 Sources of Error

All chemical analyses are subject to error, as are experimental procedures. In the case of the hydrogasification reactor, because it is a continuous process but operated on a very small scale for such a process, experimental errors are larger than is often the case.

However, this reactor has been operated for over five years as a pyrolysis reactor, so that its degree of reproducibility is well known. In general, the yield of any product can be assumed to be reproducible to within ±5% of its stated value. This estimate is borne out by material balance closures of the order of 100% ±5%. Most of the yield data are reproducible to ±2%.

In catalytic work, an apparent lack of precision in experimental results is frequently not inherent in the measurements, but is only a reflection of the difficulty of achieving reproducible performance from a catalyst in different experiments. This factor is not thought to be serious in the present work, and replicate runs usually gave only normal scatter in results.

Analyses of specific components is subject to the normal errors in gas chromatography, which vary somewhat with the detection system and its response factors. In general, all gaseous products were measured with an accuracy of no worse than ±5% for minor components and ±2% for major components, with the exception of water. Water yield is always difficult to determine accurately and errors of 10% to 20% in values obtained are possible.

4. RESULTS AND DISCUSSION

4.1 Introduction

Because this was a preliminary investigation, much of the experimental work was sequential as the understanding of the process behaviour evolved. Therefore, it is more appropriate to discuss each set of results in turn, as they are presented.

During this study IEA Poplar standard sawdust was used as the biomass feed for the hydrogasification process. This sawdust was ground and a sized fraction between 105-250 μm was used to feed into the reactor. The gasification experiments were numbered as G-(number). The mass balance of all the experimental runs was calculated using a computer program which produced a summary sheet of results. These summary sheets are available in the MASc thesis of M. Garg. These data were used to prepare all the Tables and Figures used to compare various product yields. Some experiments which gave poor mass balances were discarded and are not included in the final summary sheets. A sample log sheet of experimental data for Run G-13, together with a detailed sample calculation and a summary sheet for this run are given in the Appendix.

Some terms will be frequently used during this discussion. These terms are defined below.

Residence Time - The residence time of gases and vapors in the reactor. It is calculated by dividing the net empty volume of the reactor by the gas volumetric flow rate at reactor conditions.

F/C Ratio - F/C ratio is the amount of moisture free wood fed per hour per unit mass of catalyst.

Reformable Carbon in Gas - The percentage of carbon present in gas, not associated with CO_2.

Selectivity for CH_4 - The percentage of gas carbon associated with methane.

SCMof CH_4/Feed - The amount in standard cubic meters of methane produced per unit mass of moisture free feed.

HHV Gas/Feed - The ratio of higher heating value (HHV) of gas to that of moisture free feed. HHV of gaseous product was calculated by assuming total combustion of CO and of gaseous hydrocarbons.

4.2 Preliminary Experiments

Scott et al. (1985) have extensively studied the pyrolysis of poplar wood and other biomass materials in a fluidized bed bench scale reactor containing Ottawa sand and employing a nitrogen atmosphere. This study was mainly directed towards maximizing the liquid yield. The gas yields were generally low and the product gas mixture contained mainly CO, CO_2 and CH_4. Particularly, the yield of CH_4 was very low. Typical results for the pyrolysis of poplar wood are given in Table 4.1 (Run 25), taken from those reported by Scott and Piskorz (1984). As an initial test in this work, poplar wood was pyrolyzed in a hydrogen atmosphere in a fluidized bed of silica sand particles, using the same apparatus and procedures as Scott et al. (1985). The yield of products obtained in this experiment (Run G-42) are compared in Table 4.1 with the yield of products obtained during the pyrolysis process. The production of char, water and gaseous products was increased and the production of tar was decreased under a hydrogen atmosphere but a yield of only 1.63% of CH_4 and a 23.52% total yield of gases could be obtained.

Table 4.1 also shows the results reported by Scott et al. (1985) of a run at 500°C in a hydrogen atmosphere (Run 86), but employing a commercial nickel catalyst as

Table 4.1

PYROLYSIS OF WOOD
IEA Standard Poplar Wood, Ottawa Sand.

RUN NO.	25* Pilot Plant	G-42 Bench Unit	86** Bench Unit
Reactor Atmosphere	Nitrogen	Hydrogen	Hydrogen
Temperature, °C	541	550	500
Residence Time, s	0.54	0.37	0.44
Feed Rate, kg/hr	1.28	0.11	0.030
Bed Material	Sand	Sand	Catalyst
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)			
Tar	65.65	51.87	Tr.
Char	8.99	9.34	2.5
Water	7.4	14.91	25.3
Total Gas	21.22	23.52	74.5
CO	10.47	10.66	4.82
CO_2	8.64	8.24	13.16
CH_4	1.28	1.63	56.48
H_2	0.06	-	
TOTAL YIELD	101.3	99.6	102.0

* Scott and Piskorz (1984)
** Scott et al. (1985)

the fluidized solid in place of sand. It is apparent that it appears to be possible to methanate the wood to a very high degree in a hydrogen atmosphere at 101 kPa abs. pressure, given a sufficiently active and appropriate catalyst. This result and similar ones reported by Scott et al. represent the primary discovery on which the present study is based.

Preliminary experiments were also carried out using four different nickel catalysts on alumina supports in order to select the most suitable for more detailed study. Three catalysts, G-33RS, G-65RS and G-65, were received from "United Catalysts Inc.". One Ni/Al203 catalyst was prepared in-house. The composition and physical properties of these catalysts and of the alumina support are given in Table 4.2 as supplied by the manufacturer. The surface area of one of these catalysts (G-65RS) was checked in our laboratory by BET nitrogen adsorption, and good agreement with the quoted surface area value was obtained. The two industrial nickel catalysts (G-33RS and B-65RS) contained about 4% carbon. This carbon was found to cause a major difficulty in closing the carbon balance of the experiments. During the reduction step, the collected gases showed the presence of methane and CO_2. In some earlier experiments, gases were not collected during

Table 4.2

United Catalysts Inc.

Typical Chemical and Physical Properties

METHANATION CATALYST

Effective: 7/25/83
Supersedes: 1/31/78

CATALYST G-33RS:

Catalyst Type G-33RS
Catalyst Form ..... Tablets
Catalyst Size ..... 1/4" x 1/4"

Chemical Composition	Weight %
Ni*	36 ± 2
S	<0.05
C	3-5
% Reduction (minimum)	40

Physical Properties

A. Bulk Density, lbs./Cu.Ft..... 65 ± 5

B. Surface Area, m^2/g 45-75

C. Pore Volume, cc/g >29.2 Angstroms 0.25-0.35

D. Crush Strength, Minimum Average* ..... 20 lbs.
No More Than 5% Less Than ..... 10 lbs.

*Properties normally measured by Quality Control.

CATALYST G-65RS:

Catalyst Type G-65RS
Catalyst Form ..... Extrusions
Catalyst Size ..... 3/16"

Chemical Composition	Weight %
Ni*	25-29
Al_2O_3	55-65
CaO	4-8
SiO_2	<0.30
C (As Graphite)	3-5
S*	<0.05
Na*	<0.30
Other Heavy Metals	<0.10
Reduction (Minimum)*	40.0

Physical Properties

A. Bulk Density, lbs./Cu.Ft ..... 55 ± 5

B. Crush Strength, lbs. per mm Length
Minimum Average* 5

C. Surface Area, m^2/g 35-65

D. Pore Volume, cc/g >29.2 Angstroms 0.30-0.40

E. Particle Size:
Normal Length, Millimeters 10-13
No More Than 5% Less Than 4

*Properties normally measured by Quality Control.

Table 4.2 (cont'd)

Catalyst G-65 :

Catalyst type	G-65
Catalyst form	Extrusions
Catalyst size	1/8"
Nominal content :	
	weight %
Nickel	25
Refractory	Balance

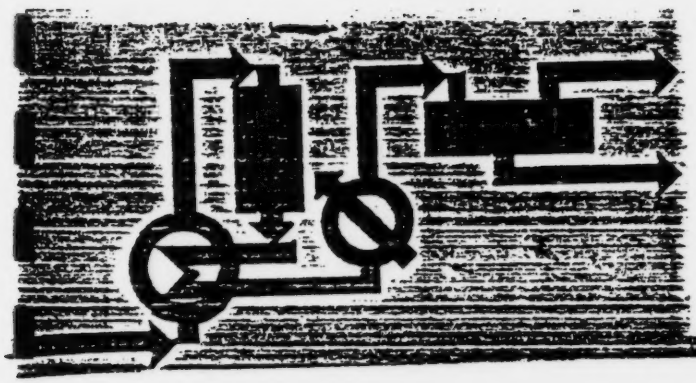
Catalyst Lab (1) :

Chemical composition	weight %
Nickel	13
Alumina	Balance

Physical properties

Surface area (for particles in the size range 250-590 um)	207 m2/g
Pore size, A	20 - 500

Note : All the industrial catalysts were crushed to a required size range and then used for experiments. All the physical properties are for the particular form and size of the catalyst, as received from the industry.



HARSHAW CATALYSTS

DATA SHEET

ALUMINA CATALYST Al-1404 T

Alumina Catalyst Al-1404 T is a highly active tabletted alumina support. Alumina's generally are used for hydration/dehydration reactions or as a catalyst support.

Typical Properties	T 1/8"	T 3/16"
LOI @ 650°C	3.5	3.5
Surface Area, m^2/g	165	160
Packed ABD	0.87	0.92
Avg. Strength	20 lbs.	45 lbs.

Alumina Tablets

	Surface Area m^2/g	Pore Volume cc/g	Packed ABD lbs/ft³	Crush Strength lbs	Al_2O_3 %	Fe_2O_3 %	SiO_2 %	Na_2O %
Al_2O_3								
Al-4183 T 1/8"	200	1.00	28	13	99+	0.03	0.09	0.01
Al-4028 T 1/8"	252	0.79	32	14	98+	0.05	0.3	0.04
Al-1404 T 1/8"	161	0.43	53	18	98+	0.03	<0.1	0.03
Al-3438 T 1/8"	186	0.46	53	15	99	0.01	0.01	0.01
Al-0104 T 1/8"	90	0.38	62	11	98+	0.03	<0.1	0.33
Al-3980 T 1/8"	4	0.27	73	28	99+	0.01	0.01	0.01
Al_2O_3 WITH SILICA								
Al-1602 T 1/8"	220	0.60	50	20	91+	0.03	6.5	0.05

These materials can be supplied as activated gamma through alpha aluminas and with varied surface area, pore volume, crush strength and silica content.

GBM 1179

The Harshaw Chemical Company
Catalyst Department
23800 Mercantile Road
Beachwood, Ohio USA 44122

Harshaw Chemie B.V.
Postbus 19
Demeern, Netherlands
Phone: (03406) 2244

the reduction process, so it was difficult to get good material balances for these runs. When experiments were carried out with the catalyst prepared in-house, which was free of carbon, it gave quite similar yields of the gaseous products to those obtained from the industrial catalysts. A good material balance was also achieved. It was decided, therefore, to use the nickel catalysts prepared in this laboratory in all future tests.

Nickel content of the catalysts was determined by gravimetric analysis using an alcoholic solution of dimethylglyoxime as described in the previous section.

Table 4.3 presents the results of the experiments with G-65 and G-65RS catalysts. Runs G-3, G-4 and G-8 were carried out with G-65RS catalyst at temperatures of 450°C, 500°C and 550°C respectively. A total of 70% carbon gasification was achieved and the production of CO_2 was also very low (2.4%). Runs G-3 and G-4 were carried out at a residence time of 0.6 s. The residence time was defined as the space volume in the reactor divided by the gas volumetric flow rate at reactor conditions. In Run G-8, in spite of the high temperature, carbon conversion to gaseous products remained at 70% but the production of CO_2 increased to

Table 4.3

Results of Experiments with G-65 and G-65RS Ni Catalysts

RUN NO.	G-3	G-4	G-8	G-12
Catalyst no.	G-65RS Fresh	G-65RS Fresh	G-65RS Fresh	G-65 Fresh
Catalyst Ni %	27.00	27.00	27.00	25.00
Temperature,°C	450.00	500.00	550.00	565.00
Residence Time, s	0.60	0.59	0.72	0.40
Total Feed, g	28.81	28.21	51.74	33.49
Feed Particle, um	250-590	250-590	105-250	105-250
Moisture %	5.22	5.22	4.32	4.32
Catalyst Wt., g	50.06	50.20	50.50	39.79
Catalyst Particle,um	250-590	250-590	105-250	250-590
Total Run Time, min	30.00	30.00	26.00	24.00
F/C , l/hr	1.10	1.10	2.30	1.40
TOTAL YIELD OF COMPONENTS,(% WT. OF FEED, MF)				
CO	0.76	1.16	13.98	6.21
CO2	1.22	2.37	22.72	8.08
CH4	34.50	44.56	28.82	45.41
C2H4	0.01	0.00	0.07	0.34
C2H6	0.01	0.01	0.05	0.20
C3	0.01	0.00	0.13	0.14
C4+	0.07	0.01	0.12	0.06
Total Gas	36.58	48.11	65.90	60.44
Char	10.57	9.26	9.12	10.29
Tar	4.24	0.79	7.16	1.26
Water	42.22	44.30	18.28	39.64
TOTAL YIELD	93.61	102.46	100.46	111.62
TOTAL CARBON YIELD	104.09	110.29	112.01	108.55
TOTAL GAS CARBON	54.36	70.63	70.34	81.52
CARBON IN CH4	52.86	68.26	44.57	70.23
SCM CH4/FEED	(b) 0.52	0.67	0.44	0.69
REFORMABLE C IN GAS	(b) 99 %	98 %	82 %	94 %
SELECTIVITY FOR CH4	(b) 97 %	97 %	63 %	86 %
HHV GAS/FEED	(b) 0.99	1.28	0.90	1.34

22%. This increase in CO_2 may be related to the longer residence time of 0.72 s during this run. Run G-12 was carried out with G-65 catalyst at 565°C and the low residence time of 0.40 s. The gaseous carbon conversion of 81% achieved with CO_2 production of 8% was the highest of these runs, as was the conversion to CH_4.

Table 4.4 presents the results of Runs G-5, G-6 and G-7 using G-33RS catalyst. All these runs were carried out at about the same temperature but there was a small difference in the residence time between Run G-5 (0.55 s) and Run G-6 (0.48 s). Run G-7 was a repeat of Run G-6. A good agreement was observed in the carbon conversion to gas and in the methane yields from these runs.

Table 4.5 shows the results of two experiments which were carried out using Lab (1) catalyst (contained 13% nickel) prepared in this laboratory. Runs G-9 and G-11 were performed at temperatures of 530°C and 540°C, respectively. Deactivated catalyst from Run G-9 was regenerated and used for Run G-11. No appreciable difference was found between the gasification products from these runs which suggests that the catalyst may be regenerated and used two or more times without any significant change in the gasification products.

Table 4.4

Results of Experiments with G-33RS Ni Catalyst

RUN NO.		G-5	G-6	G-7
Catalyst no.		G-33RS Fresh	G-33RS Fresh	G-33RS Fresh
Catalyst Ni %		36.00	36.00	36.00
Temperature,°C		500.00	520.00	510.00
Residence Time, s		0.55	0.48	0.48
Total Feed, g		29.17	42.47	42.25
Feed Particle, um		250-590	105-250	105-250
Moisture %		5.22	4.32	4.32
Catalyst Wt., g		50.00	50.08	50.15
Catalyst Particle,um		250-590	250-590	250-590
Total Run Time, min		30.00	30.00	30.00
F/C ; 1/hr		1.10	1.60	1.60
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)				
CO		1.44	3.59	4.39
CO2		1.84	5.05	5.73
CH4		44.42	40.15	43.39
C2H4		0.01	0.02	0.02
C2H6		0.01	0.01	0.01
C3		0.00	0.03	0.00
C4+		0.00	0.03	0.00
Total Gas		47.71	48.87	53.54
Char		6.91	7.23	10.34
Tar		1.93	6.51	2.82
Water		45.89	36.65	35.22
TOTAL YIELD		102.44	99.25	101.92
TOTAL CARBON YIELD		106.91	99.06	106.71
TOTAL GAS CARBON		70.36	68.25	74.25
CARBON IN CH4		66.05	62.09	67.10
SCM CH4/FEED	(b)	0.67	0.61	0.66
REFORMABLE C IN GAS	(b)	99 %	96 %	96 %
SELECTIVITY FOR CH4	(b)	97 %	91 %	90 %
HHV GAS/FEED	(b)	1.27	1.16	1.26

Table 4.5

Results of Experiments with Lab (1) Ni Catalyst

RUN NO.		G-9	G-11
Catalyst no.		LAB (1) Fresh	LAB (1) Regenerated
Catalyst Ni %		13.00	13.00
Temperature, °C		530.00	540.00
Residence Time, s		0.46	0.42
Total Feed, g		47.28	26.89
Feed Particle, um		105-250	105-250
Moisture %		4.32	4.32
Catalyst Wt., g		44.52	44.73
Catalyst Particle,um		250-590	250-590
Total Run Time, min		33.00	24.00
F/C , 1/hr		1.80	1.40
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)			
CO		5.84	8.22
CO2		5.89	4.97
CH4		38.01	38.56
C2H4		0.05	0.08
C2H6		0.04	0.07
C3		0.23	0.15
C4+		1.09	0.19
Total Gas		51.15	52.23
Char		11.06	11.01
Tar		6.63	3.25
Water		36.64	35.85
TOTAL YIELD		105.48	102.34
TOTAL CARBON YIELD		97.67	99.58
TOTAL GAS CARBON		69.66	70.51
CARBON IN CH4		38.78	39.63
SCM CH4/FEED	(b)	0.57	0.58
REFORMABLE C IN GAS	(b)	95 %	96 %
SELECTIVITY FOR CH4	(b)	84 %	85 %
HHV GAS/FEED	(b)	1.15	1.15

While the results obtained with the commercial catalysts appear to be slightly better than those obtained from the in-house Lab (1) catalyst, the commercial catalyst did contribute some gas products from the carbon incorporated in the catalyst. If all the carbon in the catalyst formed CH_4 or CO, the error from this source in reported yields of CO or CH_4 could have been as high as 20% to 25%. The G-65 catalyst, although it also contained carbon, gave a good performance, however. The problem of not knowing the exact composition or nature of a particular commercial catalyst, together with the comparable performance of our own Lab (1) catalyst, led to the decision to use catalysts prepared in our own laboratory. Use of these catalysts also allowed investigation of support activity and metal-content effect as independent parameters.

4.3 Effect of Nickel Content of the Catalyst

Experiments were carried out with four catalysts containing different amounts of nickel. All these nickel catalysts were prepared in this laboratory using alumina (Al-1404, Harshaw) as support. The reaction conditions and the results of these experiments are given in Table 4.6. Three catalysts were used at 550°C whereas Lab (2) Ni catalyst (containing 17% nickel) was used at 560°C. F/C ratio was in the range of 1.12

Table 4.6

EFFECT OF NICKEL CONTENT OF CATALYST
Residence Time 0.44 s

RUN NO.	G-44	G-28	G-13	G-45
Catalyst description	Lab(4)Ni	Lab(3)Ni	Lab(2)Ni	Lab(5)Ni
Catalyst Ni %	3.0	8.8	17.0	30.0
Temperature, °C	550	550	560	550
F/C RATIO, l/hr	1.12	1.69	1.41	1.22
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)				
CO	20.91	6.21	5.32	4.51
CO_2	10.79	7.34	5.00	2.77
CH_4	19.63	42.27	44.78	46.21
C_2H_4	0.34	0.03	0.00	0.03
C_2H_6	0.31	0.02	0.00	0.03
C_3	0.62	0.06	0.00	0.08
C_4^+	0.85	0.07	0.00	0.25
Total Gas	53.46	55.99	55.10	53.88
Char	17.36	10.70	9.01	6.64
Tar	3.07	0.98	1.33	1.75
Water	32.39	39.81	41.63	46.15
TOTAL YIELD	106.28	107.48	107.07	108.42
REFORMABLE GASES	42.67	48.65	50.10	51.11
TOTAL GAS CARBON	58.54	75.28	76.76	77.68
CARBON IN CH_4	30.36	65.37	69.25	71.47
REFORMABLE C IN GAS	90 %	95 %	96 %	98 %
SELECTIVITY FOR CH_4	52 %	87 %	90 %	92 %
HHV GAS/FEED	0.72	1.24	1.30	1.35
TOTAL MOLES OF GAS PRODUCED PER kg OF WOOD	22.71	30.34	31.02	31.21

to 1.69 for all these experiments. As shown in Figure 4.1, the char yield decreased with the increase in the nickel loading on the catalyst. The tar yield was in the range of 1% to 3% for all four catalysts, indicating that all these catalysts are active enough to crack most of the tar during the hydrogasification process.

Although total gas production changed very little with Ni content, the production of CO and CO_2 decreased and the production of CH_4 increased with the increase in nickel loading on the catalysts. The total moles of reformable gas produced per kg of feed (mf) also increased initially with the increase in the nickel content of the catalyst. The changes in the production of total gas and of the key components are shown in Figure 4.2.

The total conversion of feed carbon to gaseous products was only 58.5% with the 3% nickel catalyst but all other nickel catalysts gasified more than 75% of feed carbon. As shown in Table 4.6, a sharp increase was observed in the carbon conversion to CH_4 with all catalysts containing 8.8% nickel or more. The selectivity for CH_4 jumped from 52% with 3% nickel catalyst to 87% with 8.8% nickel catalyst. The HHV ratio of gas

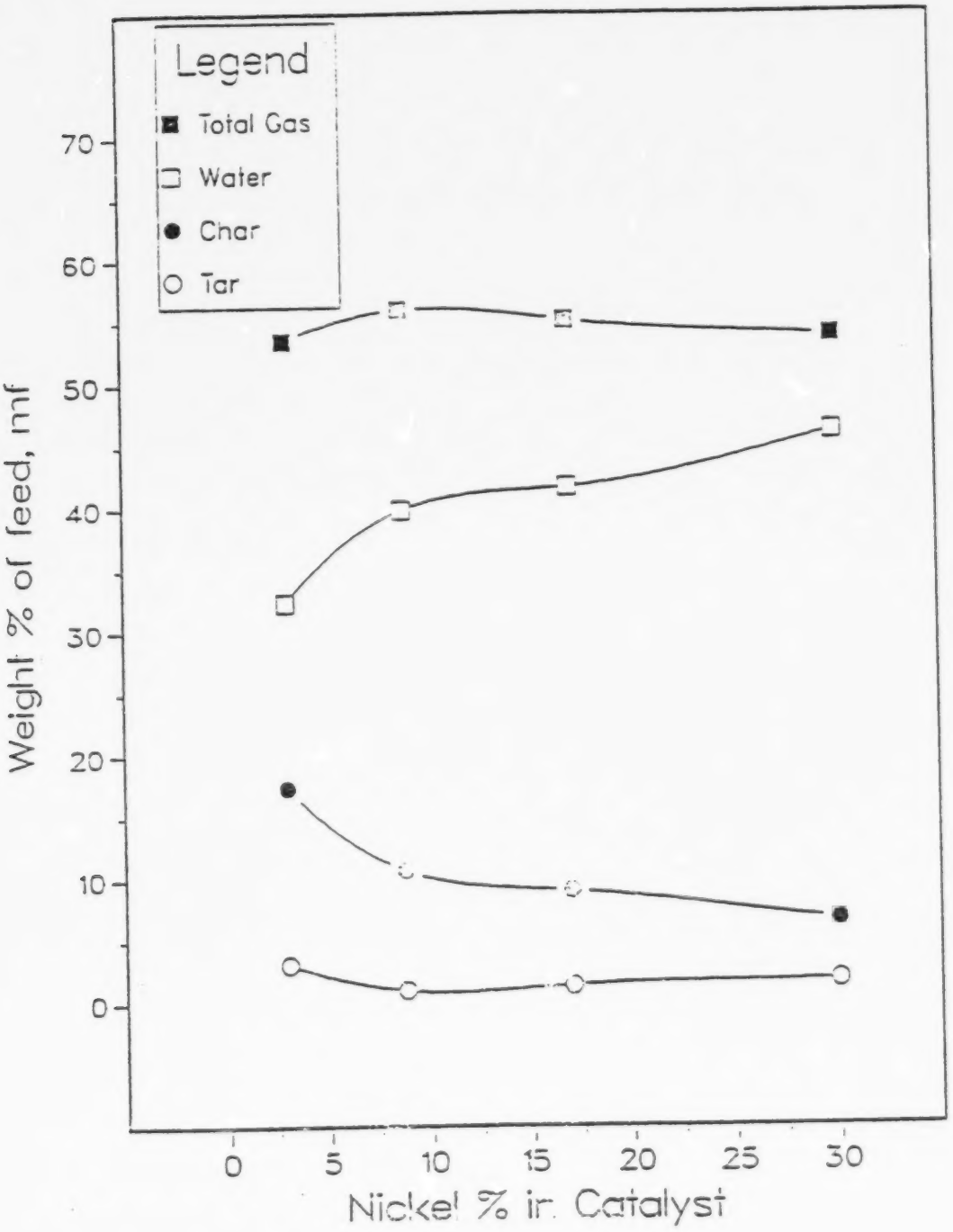


Figure 4.1 Effect of Nickel % in the Catalyst on Gasification Products, 550°C, H_2 Atmosphere, 0.44 s

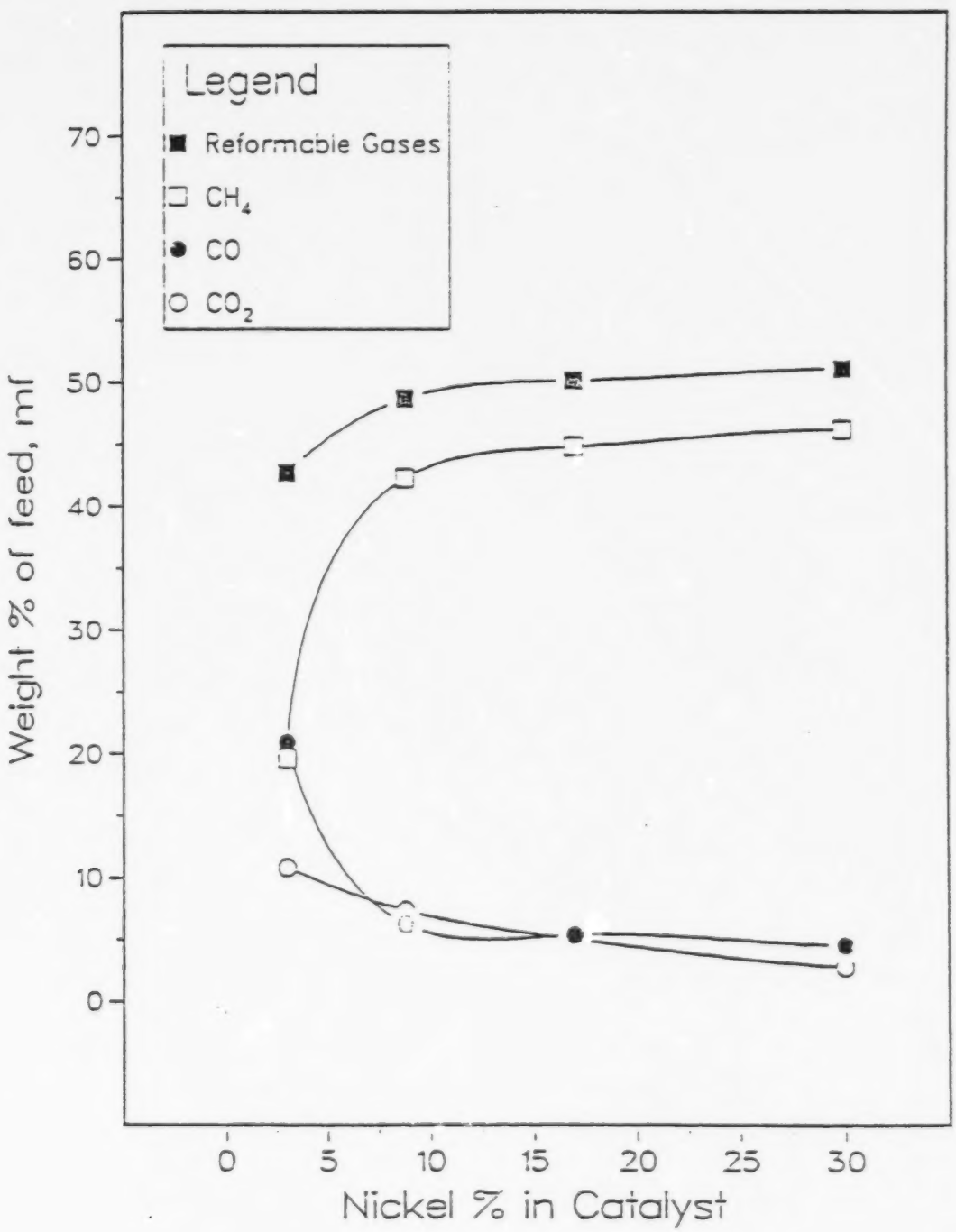


Figure 4.2 Effect of Nickel % in the Catalyst on Gaseous Products, 550°C, H_2 Atmosphere, 0.44 s

to wood also increased from 0.72 with 3% nickel catalyst to 1.24 with 8.8% nickel catalyst.

More than 8.8% nickel on alumina marginally improved the cracking and reforming activity of the catalyst. Therefore, a catalyst containing a minimum of 8.8% nickel on alumina support may be considered suitable for the hydrogasification process.

4.4 Effect of Hydrogen Atmosphere on Nickel Catalyst

Experiments were carried out in H_2 and N_2 atmospheres in the presence of a nickel catalyst in the fluidized bed in order to demonstrate the necessity for a hydrogen atmosphere if a high degree of gasification is to be achieved.

Results of Run G-43 and G-38 are presented in Table 4.7. Hydrogen was used as the fluiding gas and the feed carrier gas for G-38, whereas, nitrogen gas was used in place of hydrogen for G-43, Both runs were carried out at 550°C and at similar F/C ratios (3.2 1/hr for G-43 and 2.9 1/hr for G-38). The production of CO and CO_2 was close to twice as great with nitrogen gas atmosphere as with hydrogen. CH_4 yield was 29% with a hydrogen atmosphere but only 5.55% CH_4 was produced with nitrogen, suggesting that the CH_4 production is dependent upon hydrogen partial pressure and CO

Table 4.7

EFFECT OF HYDROGEN PARTIAL PRESSURE ON GASIFICATION PRODUCTS ON NICKEL CATALYST
Lab(5) Ni Cat. (30% Ni), 550°C.

RUN NO.	G-43	G-38
Reaction Atmosphere	Nitrogen	Hydrogen
Residence Time, s	0.61	0.44
F/C RATIO, l/hr	3.19	2.90
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)		
CO	27.40	15.36
CO_2	27.51	14.56
CH_4	5.55	29.08
$C_2 - C_4$	1.58	0.93
Total Gas	62.02	59.94
Char	16.49	10.94
Tar	12.91	6.18
Water	6.37	29.48
TOTAL YIELD	97.79	106.54
TOTAL REFORMABLE GASES	34.51	45.38
TOTAL GAS CARBON	50.94	68.34
CARBON IN CH_4	8.58	44.98
REFORMABLE C IN GAS	70 %	88 %
SELECTIVITY FOR CH_4	17 %	66 %

may be one of the primary sources of CH_4 production. Lower yields of char and tar with a hydrogen atmosphere indicate that hydrogen assists in the cracking of tar to gaseous products which in turn yield CH_4 and which also appears to reduce the char production. Only 6.37% water was produced with nitrogen whereas the water production of 46.15% was obtained with hydrogen. In this case also, the low production of water with nitrogen could be due to high CO and CO_2 production and low hydrogen partial pressure.

Comparison of the results for the two runs shown in Table 4.7 suggests strongly that the cracking activity of the catalyst is fairly high, as is apparent by comparing run G-43 in Table 4.7 to Run 25 in Table 4.1, in which sand was used. Comparison of Run G-38 and Run G-42, both in hydrogen atmospheres but using catalyst and sand respectively, shows the necessity for both the cracking activity and the presence of hydrogen to allow a high degree of gasification.

4.5 Effect of Temperature

Six experiments were carried out, in the range of 400°C to 650°C, to study the effect of temperature on the gasification products. Lab (2) Ni catalyst containing 17% nickel on alumina was used for all these

experiments and the residence time of the gaseous products in the reactor was also kept about the same (0.43 s to 0.45 s).

Table 4.8 and Figure 4.3 give the yield of different gasification products at temperatures between 400°C and 650°C. No significant decrease was observed in the production of tar above 500°C and the char yield also remained approximately constant above 550°C. A sharp decrease in water production, above 550°C, appears to be related to the increased yields of CO and CO_2. High production of CO and CO_2 accounted for most of the feed oxygen and, therefore, reduced the water production. Comparison of results, given in Table 4.8, for experiments at 560°C and 650°C shows a six-fold increase in the production of CO (from 5.32% to 31.66%) at higher temperatures, whereas the CO_2 production increased about 100% (from 5.0% to 10.31%). The production of CO and CO_2 at different temperatures are plotted in Figure 4.4. These results appear to show that hydrogenation activity of the nickel, either to form CH_4 (from CO) or H_2O (from organics or from the shift reaction) is much reduced at temperatures above 600°C, or else the methane-steam reaction and the shift reaction are accelerated above 600°C. Since the amount of total gas carbon is relatively constant above 600°C, it is

Table 4.8

EFFECT OF TEMPERATURE ON GASIFICATION PRODUCTS
Lab(2) Ni Cat., 17% Nickel, Res. Time 0.43-0.45 s

RUN NO.	G-20	G-15	G-14
Temperature, °C	400	450	500
F/C RATIO, l/hr	1.83	1.19	1.45
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)			
CO	3.85	1.86	2.10
CO_2	5.01	1.71	1.89
CH_4	26.13	35.21	43.71
C_2H_4	0.21	0.03	0.02
C_2H_6	0.18	0.03	0.01
C_3	0.19	0.12	0.02
C_4+	0.40	0.05	0.13
Total Gas	35.96	39.01	47.87
Char	20.34	14.08	12.44
Tar	19.68	14.30	4.78
Water	27.68	36.00	46.45
TOTAL YIELD	103.66	103.39	111.54
REFORMABLE GASES	30.94	37.30	45.98
TOTAL GAS CARBON	48.28	57.45	70.82
CARBON IN CH_4	40.40	54.46	67.60
SCM CH_4/FEED	0.39	0.53	0.66
REFORMABLE C IN GAS	94 %	98 %	98 %
SELECTIVITY FOR CH_4	84 %	95 %	95 %
HHV GAS/FEED	0.79	1.02	1.26

TABLE (4.8) Continued .....

RUN NO.	G-13	G-18	G-21
Temperature, °C	560	600	650
F/C RATIO, l/hr	1.41	1.18	1.66
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)			
CO	5.32	10.80	31.66
CO_2	5.00	7.48	10.13
CH_4	44.78	44.70	30.88
C_2H_4	0.00	0.09	0.00
C_2H_6	0.00	0.05	0.01
C_3	0.00	0.07	0.00
C_4^+	0.00	0.05	0.16
Total Gas	55.10	63.24	72.84
Char	9.01	7.27	6.97
Tar	1.33	3.35	1.37
Water	41.63	33.92	19.37
TOTAL YIELD	107.07	107.78	100.55
REFORMABLE GASES	50.10	55.76	62.71
TOTAL GAS CARBON	76.76	83.33	81.72
CARBON IN CH_4	69.25	69.14	47.76
SCM CH_4/FEED	0.68	0.68	0.47
REFORMABLE C IN GAS	96 %	95 %	93 %
SELECTIVITY FOR CH_4	90 %	83 %	58 %
HHV GAS/FEED	1.30	1.34	1.05

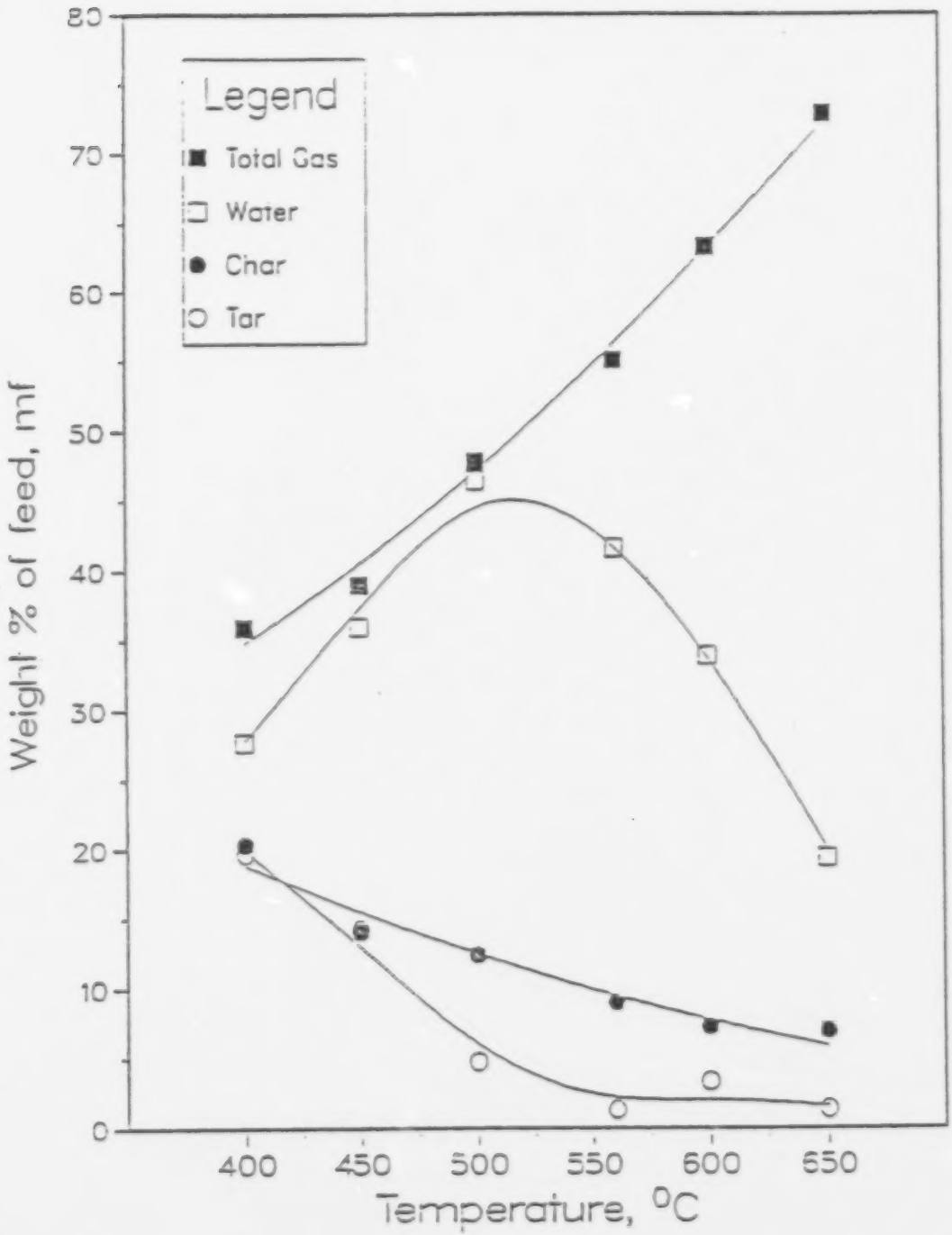


Figure 4.3 Effect of Temperature on Gasification Products Lab (2) Ni Catalyst, H_2 Atmosphere, 0.44 s

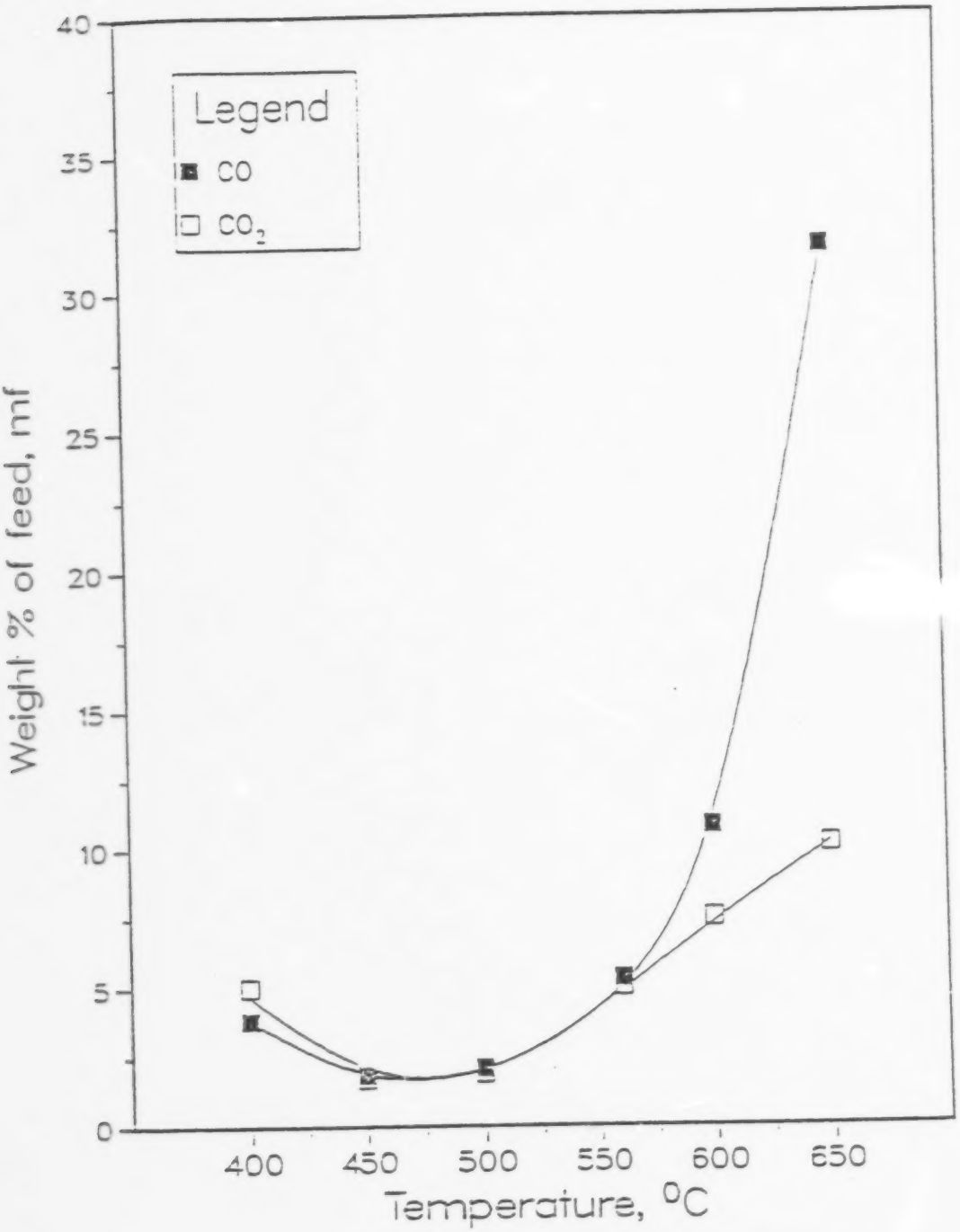


Figure 4.4 Effect of Temperature on CO and CO_2 Production Lab (2) Ni Catalyst, H_2 Atmosphere, 0.44 s

probably the latter possibility, that the reaction of CH_4 with H_2O, catalyzed by the metal, has become important. Similarly, the increased CO_2 yields at higher temperatures indicate a more rapid approach to equilibrium by the shift reaction, although the equilibrium yield itself is a little less favorable for CO_2 production.

As shown in Figure 4.5, the production of methane is favored in the temperature range of 500°C to 600°C in the presence of nickel catalyst. Similar behavior was also observed by Suzuki et al. (1984) for hydrogasification of birchwood. A temperature in the range of 500°C to 550°C was found to be better for selective methane production without producing too much CO and CO_2. The difference between the total methane production and the total gas production became significant above 550°C. It is also observed from Figure 4.6 that the selectivity for methane decreased sharply above 550°C from nearly 95% to 58% at 650°C, but the total reformable carbon (carbon in hydrocarbon gases + CO) did not change much. Therefore, the total loss in methane production could be accounted for by an increase in the production of CO. All higher hydrocarbons e.g. ethane, ethylene, etc. remained very low (below 0.2%) above 400°C.

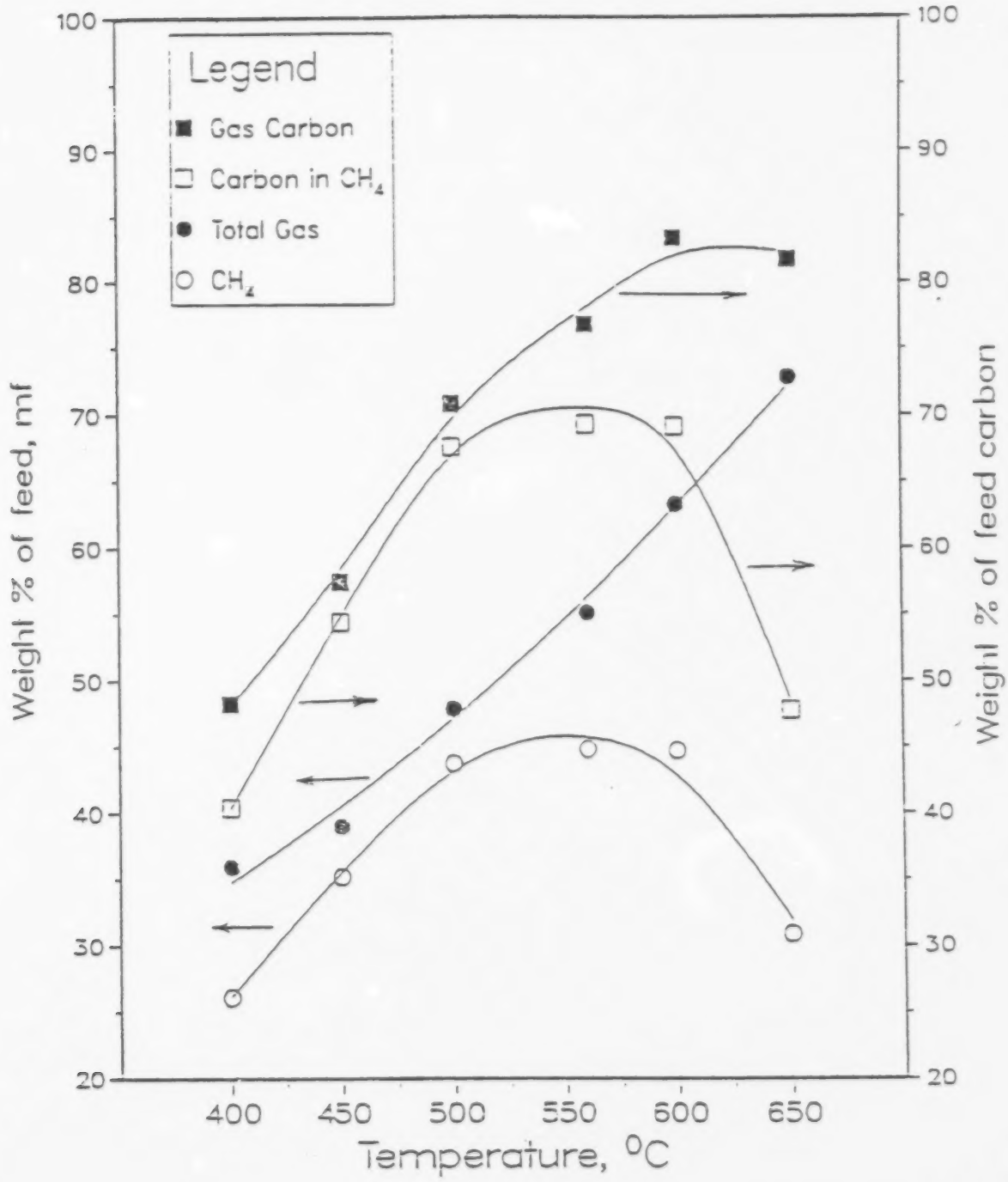


Figure 4.5 Effect of Temperature on Gas and CH_4 Production Lab (2) Ni Catalyst, H_2 Atmosphere, 0.44 s

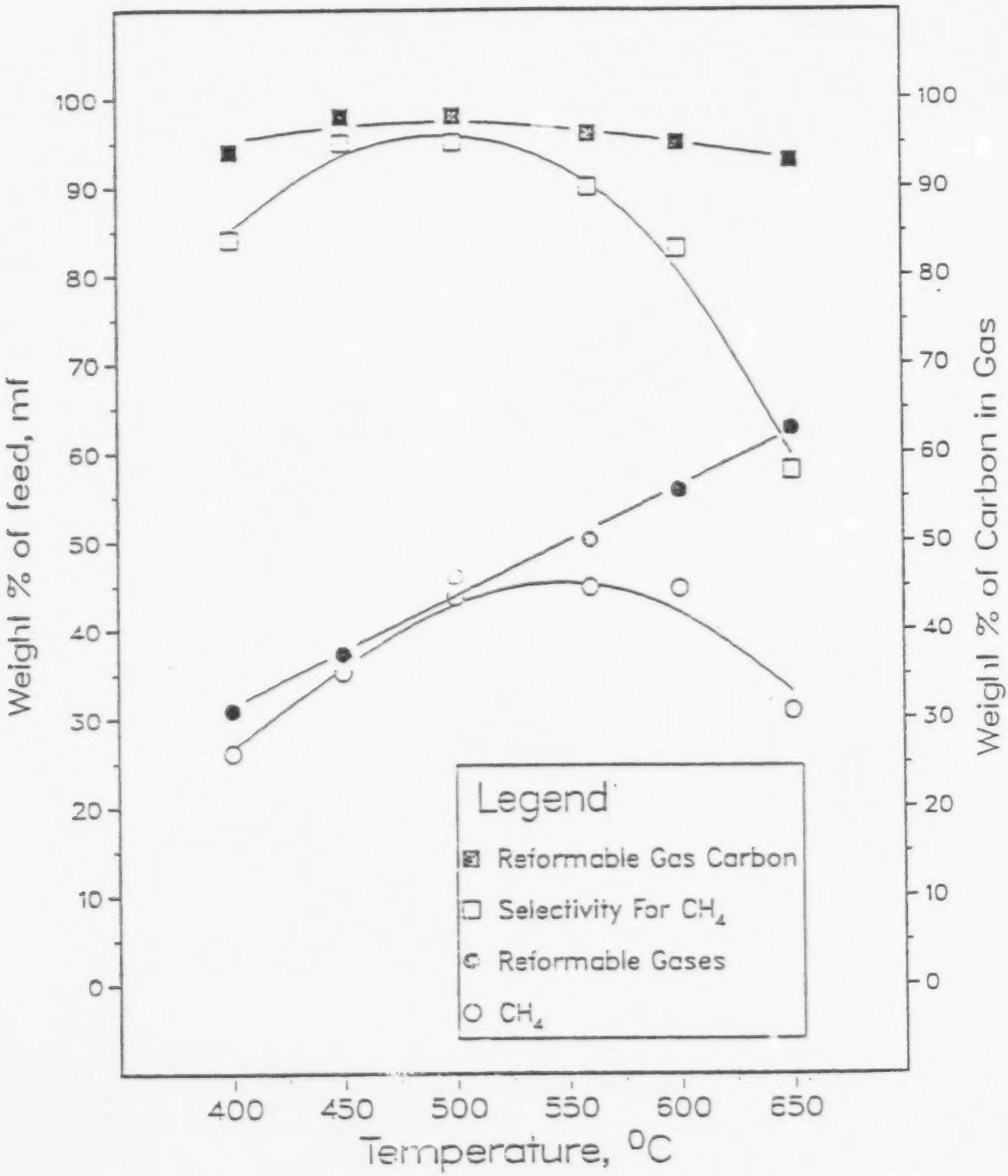


Figure 4.6 Effect of Temperature on Reformable Gas Carbon and Selectivity for CH_4, Lab (2) Ni Cat., H_2 Atmos.

At temperatures below 450°C, as shown in Figure 4.5 and Figure 4.6, the methane production as well as the selectivity for methane production decreased with temperature. At 400°C, the methane production was only 26% (% wt. of feed) with a selectivity of 84%. In terms of volume, methane was produced at the rate of 0.66 to 0.68 m^3/kg of mf-wood in the range of 500°C to 600°C. The higher heating value (HHV) ratio of product gas to wood feed increased from 0.79 at 400°C to 1.34 at 600°C, but due to high CO_2 production at 650°C, the HHV ratio decreased to 1.05.

Therefore, on the basis of the overall methane production and the selectivity for methane production, a temperature between 500°C and 550°C was found to be most favorable for the methanation of wood with nickel catalyst. In this range, about 75% of feed carbon was converted to gases, 90% to 95% of which was associated with methane, giving a 44% yield (% wt. of feed) of methane or a 67% to 69% conversion of carbon fed to CH_4 produced.

4.6 Effect of Residence Time

Two experiments were carried out at 550°C but at residence times of 0.32 s and 0.55 s, respectively. One

experiment was also done at a residence time of 0.44 s but the temperature was a little higher (560°C) than the other two experiments (550°C). As noted before, there was no significant difference in the gasification products between the temperature of 500°C to 560°C. Therefore, the yields of gasification products from these three experiments are compared in Table 4.9. More than 0.44 s residence time adversely affected the methane production and increased the production of CO and CO_2. Gas phase reactions, such as the steam-reforming of CH_4 and the water-gas shift reaction probably caused these changes in the gas composition. The selectivity for CH_4 went down from 90% at 0.44 s to 83% at 0.55 s. Therefore, a residence time of about 0.44 s or lower seems to be suitable, not only for overall gas yield but also for selective methane production.

4.7 Effect of Feed/Catalyst Ratio

The gasification products were found to be strongly dependent on the ratio of wood feeding rate to mass of catalyst particles in the bed (F/C Ratio). Two experiments, with results given in Table 4.10, were carried out using Lab (4) Ni catalyst (3% nickel) at 550°C and a residence time of 0.44 s, but the F/C ratio was 1.12 l/hr in one experiment and 3.27 l/hr for another. The production of CO and CO_2 was nearly the same during

Table 4.9

EFFECT OF RESIDENCE TIME ON GASIFICATION PRODUCTS, Lab(2) Ni Cat. (17% Ni),

RUN NO.	G-22	G-13	G-23
Temperature,°C	550	560	550
Residence Time, s	0.32	0.44	0.55
F/C RATIO, l/hr	1.87	1.41	1.89
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)			
CO	4.79	5.32	6.00
CO_2	5.45	5.00	11.74
CH_4	41.62	44.78	38.22
$C_2 - C_4$	0.39	0.00	0.01
Total Gas	52.29	55.10	55.97
Char	8.15	9.01	10.47
Tar	0.99	1.33	0.76
Water	41.46	41.63	33.02
TOTAL YIELD	102.88	107.07	100.22
REFORMABLE GASES	46.83	50.10	44.23
TOTAL GAS CARBON	72.39	76.76	71.03
CARBON IN CH_4	64.37	69.25	59.11
REFORMABLE C IN GAS	96 %	96 %	91 %
SELECTIVITY FOR CH_4	89 %	90 %	83 %

Table 4.10

EFFECT OF F/C RATIO, 550°C, 0.44 s

RUN NO.	G-44	G-37	G-45	G-38
Catalyst description	Lab(4)Ni	Lab(4)Ni	Lab(5)Ni	Lab(5)Ni
Catalyst Ni %	3.0	3.0	30.0	30.0
F/C RATIO, l/hr	1.12	3.27	1.22	2.90
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)				
CO	20.91	20.20	4.51	15.36
CO_2	10.79	10.23	2.77	14.56
CH_4	19.63	4.09	46.21	29.08
C_{2^+}	2.12	5.50	0.39	0.93
Total Gas	53.46	40.03	53.88	59.94
Char	17.36	16.81	6.64	10.94
Tar	3.07	17.15	1.75	6.18
Water	32.39	24.05	46.15	29.48
TOTAL YIELD	106.28	98.04	108.42	106.54
REFORMABLE GASES	42.67	29.80	51.11	45.38
TOTAL GAS CARBON	58.54	39.33	77.68	68.34
CARBON IN CH_4	30.36	6.33	71.47	44.98
REFORMABLE C IN GAS	90 %	85 %	98 %	88 %
SELECTIVITY FOR CH_4	52 %	16 %	92 %	66 %

both these experiments but CH_4 yield was 19.63% at the lower feed rate and only 4.09% CH_4 at the higher feed rate. The production of higher gaseous hydrocarbons was also a little higher at the high feed rate. Char production was similar during both these experiments but production of tar was considerably higher at the higher feed rate. The slightly lower production of char at higher feed rate may be due to the lower amount of tar cracked on the catalyst surface. Lower water production at high feed rate could be related to high production of tar, CO and CO_2, that is, a smaller fraction of the feed is being cracked and hydrogenated.

Two experiments were carried out using Lab (5) Ni catalyst (30% nickel). The results of these experiments are also presented in Table 4.10. The temperature and the residence time were the same for both these experiments but the F/C ratio was 1.22 l/hr for one experiment and 2.9 l/hr for another. As was the case with the 3% nickel catalyst, the fractional amount of tar and higher hydrocarbon production was high and relative CH_4 and water production was low at the higher feed rate. Also with this catalyst, the production per unit of feed of CO, CO_2 and char was high at the higher feed rate. The reason for similar CO, CO_2 and char production at both low and high wood feed rates with 3%

nickel catalyst may be the insufficient amount of nickel in the catalyst. The effect of F/C ratio was studied in greater detail using Lab (3) Ni catalyst containing 8.8% nickel.

From the results in Table 4.10, the following speculations may be made about the effect of wood feed rate and the gasification reaction mechanism:

4.7.1 The catalytic wood gasification process is controlled by surface reaction or surface adsorption equilibrium, particularly of those steps involving tar decomposition.

4.7.2 Most of the CO produced during the gasification is a primary gasification product.

4.7.3 A large fraction of the CH_4 and CO_2 is produced from CO via secondary reactions:

$$CO + 3\ H_2 \quad ==== \quad CH_4 + H_2O$$

$$CO + H_2O \quad ==== \quad CO_2 + H_2$$

4.7.4 Higher hydrocarbons are also primary gasification products which subsequently convert to CH_4 and/or CO on nickel catalyst:

$$a\ C_nH_m + b\ H_2 \quad ==== \quad x\ CH_4$$

$$C_nH_m + n\ H_2O \quad ==== \quad n\ CO + (2n+m)/2\ H_2$$

4.7.5 Some water formation is a primary pyrolysis product but the majority is a product of both the methanation process and of secondary processes during gasification, and therefore the water yield appears to depend inversely to some degree upon the extent of conversion of CO.

Four experiments at different F/C ratios were carried out using about the same amount of Lab (3) Ni catalyst (containing 8.8% nickel) and variable feed rates of wood. The results of these tests are given in Table 4.11 and Figures 4.7 to 4.9. It can be seen in Figure 4.7 that the production of gas, char and tar increases, whereas the production of water decreases, with the increase in the F/C ratio. A sharp increase in the production of tar was observed above an F/C ratio of 2.0.

Figure 4.8 shows the variation in the production of key gas components CH_4, CO and CO_2 with F/C ratio. Actual yields (wt. %) of these compounds were multiplied by the F/C ratio and then plotted on the Y-axis in order to get the production per unit time of different components per unit mass of catalyst. A sharp increase was observed in the production of CO and CO_2 per unit mass of catalyst above the F/C ratio of 1.56. However,

Table 4.11

EFFECT OF F/C RATIO ON Lab(3) Ni CATALYST
550°C, Resi. Time 0.44 s

RUN NO.	G-51	G-49	G-52	G-50
F/C RATIO, l/hr	0.84	1.56	2.27	3.68
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)				
CO	5.89	7.54	11.01	15.84
CO_2	3.08	6.74	11.60	12.95
CH_4	48.08	40.82	29.67	11.96
$C_2 - C_4$	0.41	0.38	0.97	2.94
Total Gas	57.46	55.46	53.25	43.68
Char	6.31	11.31	13.12	13.88
Tar	0.71	0.48	2.66	18.40
Water	48.91	40.33	31.95	20.26
TOTAL YIELD	113.38	107.58	100.97	96.21
REFORMABLE GASES	54.38	48.72	41.65	30.73
TOTAL GAS CARBON	81.99	74.20	63.80	44.77
CARBON IN CH_4	74.36	63.13	45.89	18.49
REFORMABLE C IN GAS	98 %	95 %	90 %	84 %
SELECTIVITY FOR CH_4	91 %	85 %	72 %	41 %
HHV GAS/FEED	1.41	1.21	0.93	0.50

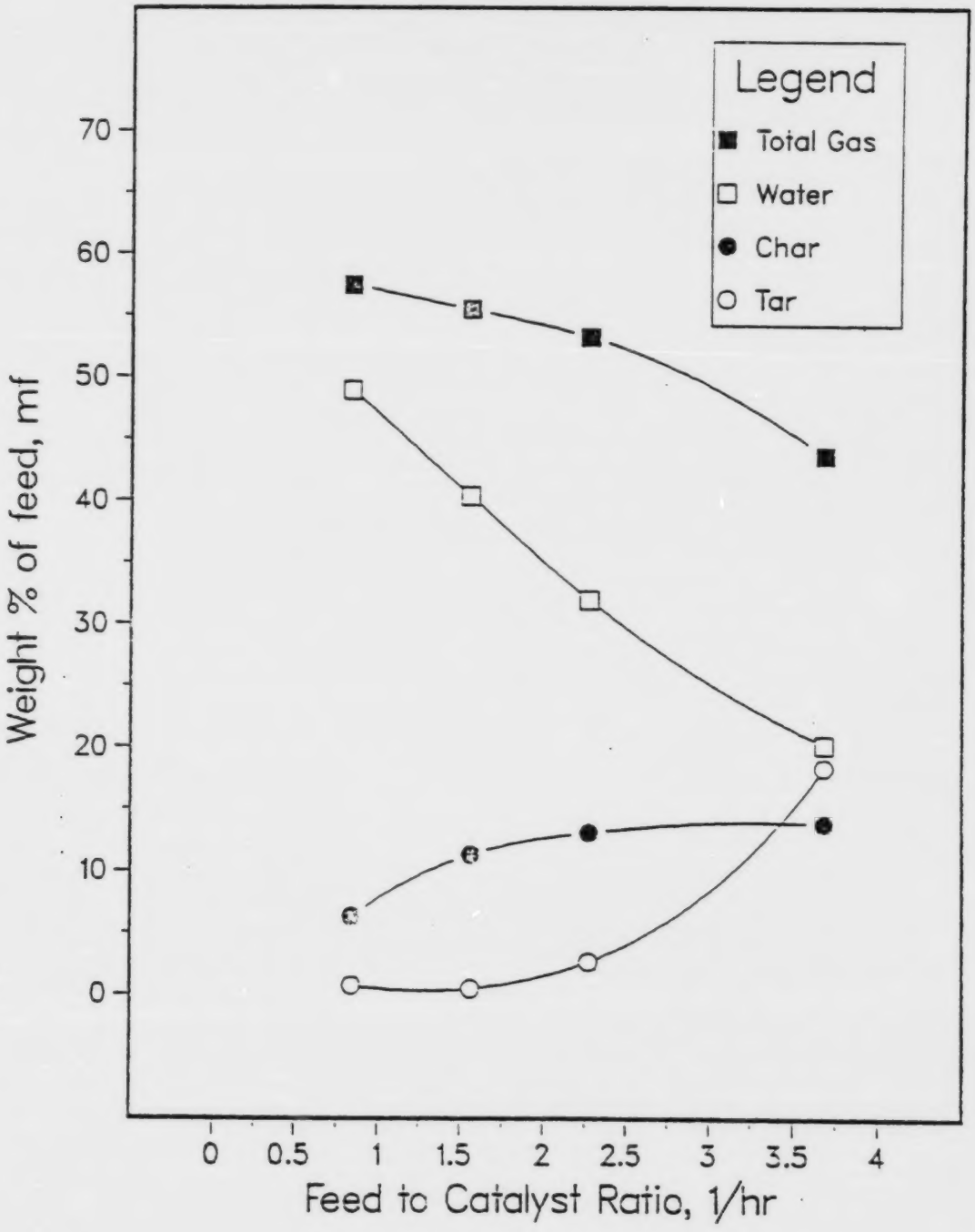


Figure 4.7 Effect of F/C Ratio on Gasification Products Lab (3) Ni Catalyst, 550°C, H_2

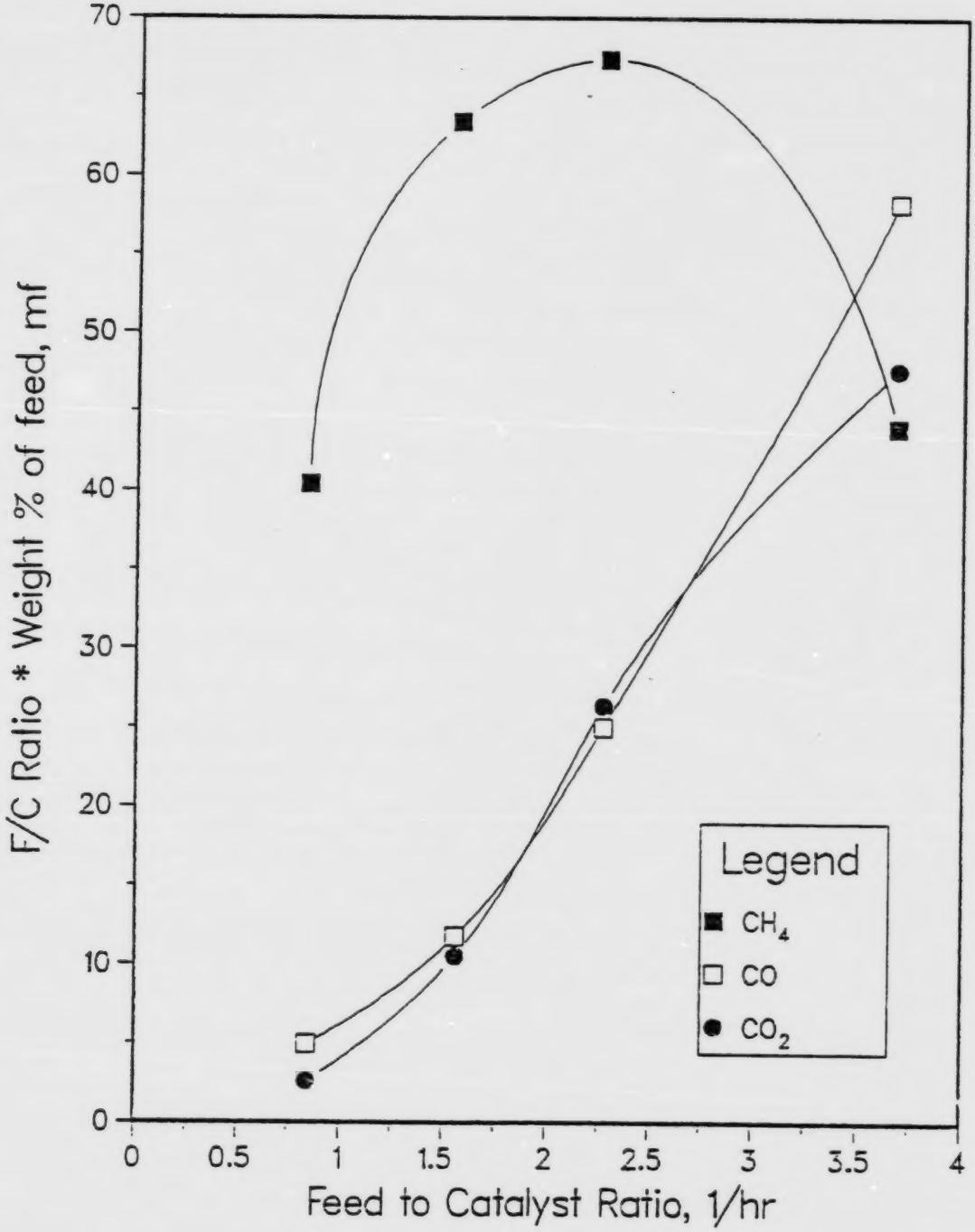


Figure 4.8 Yield of CH_4, CO and CO_2 with F/C Ratio Lab (3) Ni Catalyst, 550°C, H_2

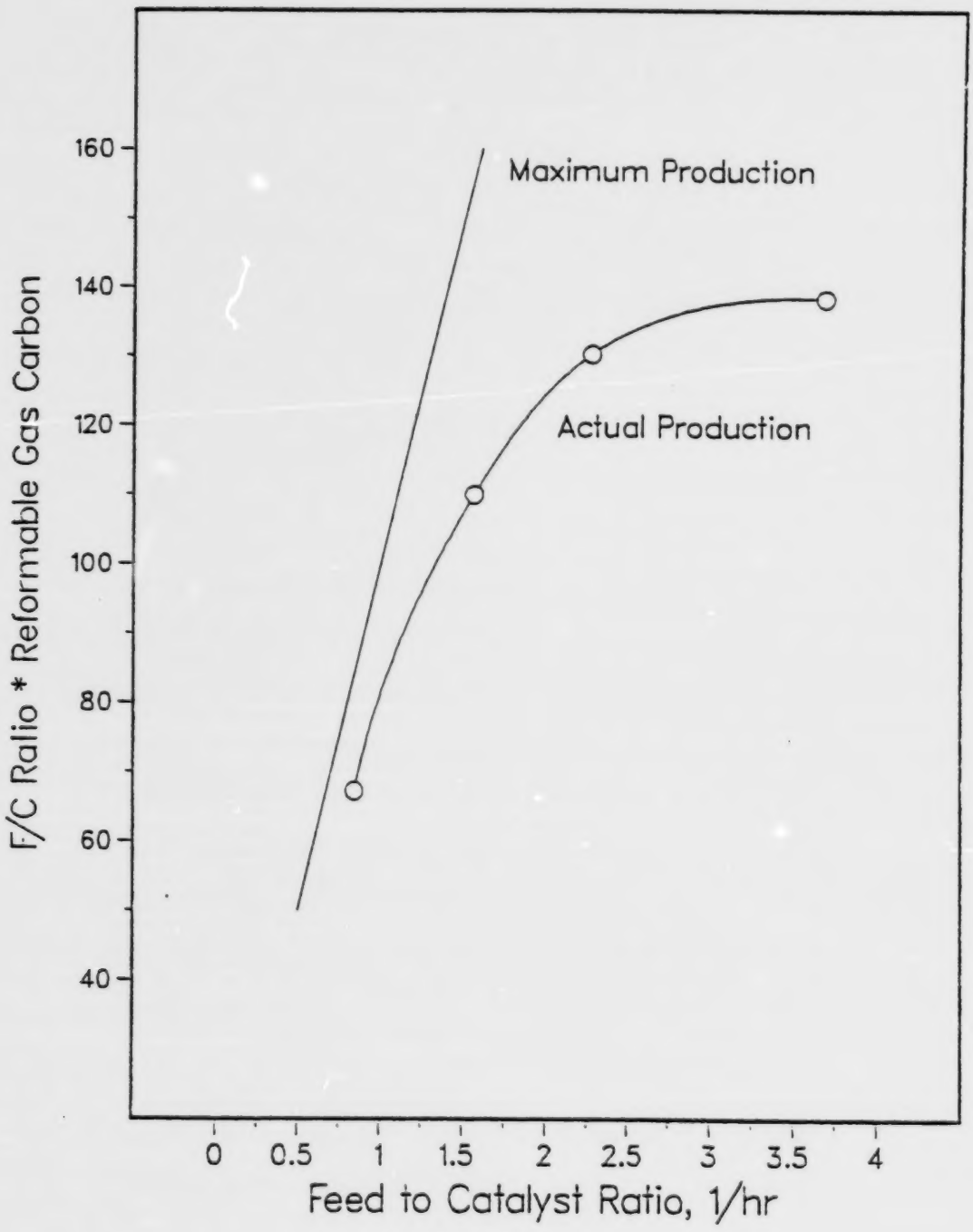


Figure 4.9 Change in Reformable Carbon in Gas with F/C Ratio Lab (3) Ni Catalyst, 550°C, H_2

the production of CH_4 remained high (greater than 0.6 g/g catalyst/hr) in the F/C ratio range of 1.56 to 3.5. The decrease in the percent feed carbon converted to CH_4 and in the selectivity for CH_4 is also evident from Table 4.11. The production of CH_4 went down from 0.73 m^3/kg of wood at F/C ratio of 0.84 l/hr to only 0.18 m^3/kg of wood at F/C ratio of 3.68 l/hr. The ratio of higher heating value (HHV) of gas to wood also decreased from 1.41 at F/C ratio of 0.84 l/hr to only 0.50 at F/C ratio of 3.68 l/hr.

In Figure 4.9, wt. % of reformable carbon in the gas was multiplied by the F/C ratio before plotting. A straight line has been drawn which assumes that all the wood carbon is converted to reformable gases at each corresponding F/C ratio. The experimental curve shows that the reformable gas carbon produced per unit time per unit weight of catalyst increased only marginally above the F/C ratio of 2.27. The gap between the ideal straight line and the experimental curve represents the sum of the total unreformable gas carbon plus the carbon in char and tar. This gap increased sharply above the F/C ratio of 1.9.

Therefore, based on Table 4.11 and Figures 4.7 to 4.9, an F/C ratio in the range of 1.56 to 1.9 is probably most suitable for the hydrogasification process and

this ratio should be kept below 2.27 with nickel on alumina catalysts. Comparing this value to the feed rates used for non-catalytic pyrolysis of wood in our pilot plant unit, for the production of a maximum liquid yield, it is very much the same, after allowing for the lower particle density of the catalyst compared to sand. Therefore, the Waterloo Fast Pyrolysis reactor would be suitable for this catalytic hydrogasification process also, particularly as the residence times and temperatures are also virtually identical for the two processes. One can speculate that because the best hydrogasification results occur at the same conditions used to obtain maximum tar yields, the gasification of the wood must proceed through the reaction of adsorbed tar molecules on the catalytic surface with adsorbed hydrogen.

4.8 Effect of the Alumina Support

In order to determine the activity of the alumina support (Al_2O_3-1404, Harshaw Chemical Co.) in the hydrogasification process, experiments were carried out using alumina particles only as the fluidized bed material in the reactor under H_2 and N_2 atmospheres. Table 4.12 shows results of these experiments which were done at 550°C and at about the same residence

Table 4.12

EFFECT OF HYDROGEN ATMOSPHERE ON THE ALUMINA SUPPORT (Al-1404, HARSHAW), 550°C, 0.44 s

RUN NO.	G-48	G-57	G-36
REACTION ATMOSPHERE	Nitrogen	Nitrogen	Hydrogen
F/C RATIO, l/hr	2.65	1.64	1.17
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)			
CO	14.41	12.83	12.95
CO_2	11.21	11.27	11.21
CH_4	2.23	2.33	2.57
Total Gas	32.04	33.02	31.28
Char	18.69	20.66	21.86
Tar	20.19	14.13	8.15
Water	21.04	22.46	28.83
TOTAL YIELD	91.96	90.26	90.12
REFORMABLE GASES	20.84	21.75	20.07
TOTAL GAS CARBON	29.63	32.49	29.47
CARBON IN CH_4	3.45	3.60	3.97
REFORMABLE C IN GAS	79 %	80 %	79 %
SELECTIVITY FOR CH_4	12 %	11 %	13 %

time. Two experiments were carried out under an N_2 atmosphere and one experiment under an H_2 atmosphere.

Under the N_2 atmosphere, F/C ratios of 2.65 and 1.64 l/hr were used. The CO and tar yields were slightly higher and CH_4 and water yields were slightly lower at high F/C ratio, suggesting that there was only a marginal effect of higher F/C ratio (at least up to 2.65 l/hr) on the cracking activity of alumina. As discussed in Section 4.7, the tar cracking activity and methanation reactions on nickel catalyst appeared to be reduced sharply above an F/C ratio of about 1.9.

One experiment was done in an H_2 atmosphere at an F/C ratio of 1.17, less than the F/C ratio during both the experiments which were carried out under N_2 atmosphere. The production of CH_4 was slightly higher and the production of tar was lower under the H_2 atmosphere than under the N_2 atmosphere which, however, because of the low feed rates, is not likely to be due to the effect of the lower F/C ratio. The general effect of an H_2 atmosphere on the product yields with alumina was very similar to the effect observed in a bed of silica sand with an H_2 atmosphere. However, the tar yields are much lower and gas and water yields are much higher for all these experiments with alumina than the yields obtained over silica sand. Therefore, the alumina

support used for the nickel catalysts appears to have considerable cracking activity, but to show no activity towards hydrogen.

4.9 Comparison of Hydrogasification with Different Solids

Three experiments were carried out using different materials (sand, alumina and a nickel catalyst) in the fluidized bed reactor under hydrogen atmosphere. The temperature was 550°C and there was only a slight difference in the residence time and F/C ratio among these experiments. As indicated in Table 4.13, the yields of all gases, char and water were higher with alumina than with sand indicating the high tar cracking activity of the alumina support. The yield of tar was probably underestimated for the experiment with alumina (Run G-36) as the total product recovery was only 90.12%, but the tar yield with alumina would still be much less than the yield of tar with sand. The product composition using sand was very different to that obtained with a fluidized bed of nickel catalyst. The tar production was 51.87% with sand but only 0.98% tar remained uncracked with the nickel catalyst. Therefore, the nickel catalyst on alumina support had a higher cracking activity than sand or alumina alone. The high yields of gaseous products and water were due

Table 4.13

HYDROGASIFICATION WITH DIFFERENT MATERIALS AT 550°C.

RUN NO.	G-42	G-36	G-28
Fluidized bed Material	Sand	Alumina Support	Lab(3) Ni Cat., 8.8% Ni
Bed particle size,um	250-300	250-590	250-590
Residence Time, s	0.37	0.44	0.44
F/C RATIO, l/hr	1.82	1.17	1.69
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)			
CO	10.66	12.95	6.21
CO_2	8.25	11.21	7.34
CH_4	1.63	2.57	42.27
C_2^+	2.97	4.55	0.18
Total Gas	23.52	31.28	55.99
Char	9.34	21.86	10.70
Tar	51.87	8.15	0.98
Water	14.91	28.83	39.81
TOTAL YIELD	99.63	90.12	107.48
REFORMABLE GASES	15.27	20.07	48.65
TOTAL GAS CARBON	21.67	29.47	75.28
CARBON IN CH_4	2.53	3.97	65.37
SELECTIVITY FOR CH_4	12 %	13 %	87 %

to cracking of nearly all of the tar with the nickel catalyst and the hydrogasification of the products. The char production was 9.34% with sand and was only a little higher with alumina or with nickel catalyst, suggesting that only a small additional fraction of char may be formed during the cracking of tar.

4.10 Effect of Catalyst Regeneration

Four experiments were carried out to study the effect of regeneration on the activity of the catalyst. The fresh Lab (2) Ni catalyst (17% nickel) was used for one experiment and then this catalyst was used for three more identical experiments after subsequent regeneration of the deactivated catalyst from the previous experiment. All of these experiments, whose results are compared in Table 4.14, were carried out at 560°C and at about the same residence time. There was a slight increase in the production of CO and CO_2 with regenerated catalysts compared to fresh catalyst. The production of CH_4 decreased somewhat for wood gasification using regenerated catalysts. The selectivity for CH_4 production was reduced from 90% to 79% after three regenerations of the catalyst, and the char yield increased from 9% to 13% for regenerated catalysts. The F/C ratio for all the experiments with regenerated catalysts was slightly more than the F/C ratio used for

Table 4.14

EFFECT OF CATALYST REGENERATION
560°C, 0.44 sec, Lab(2) Ni Cat. (17% Ni)

RUN NO.	G-13	G-26	G-27	G-32
Catalyst description	Fresh	Regen. of G-13	Regen. of G-26	Regen. of G-27
F/C RATIO, l/hr	1.41	1.64	1.58	1.76
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)				
CO	5.32	7.81	6.97	11.02
CO_2	5.00	6.62	5.77	8.40
CH_4	44.78	40.51	41.23	36.79
$C_2 - C_4$	0.00	0.08	0.14	0.30
Total Gas	55.10	55.01	54.10	56.51
Char	9.01	10.83	12.11	13.19
Tar	1.33	0.54	0.90	2.05
Water	41.63	36.79	38.83	38.88
TOTAL YIELD	107.07	103.18	105.94	110.63
REFORMABLE GASES	50.10	48.40	48.33	48.11
TOTAL GAS CARBON	76.76	73.40	73.39	71.87
CARBON IN CH_4	69.25	62.65	63.77	56.90
REFORMABLE C IN GAS	96 %	95 %	96 %	93 %
SELECTIVITY FOR CH_4	90 %	85 %	87 %	79 %

the experiment with fresh catalyst. The decrease in the CH_4 production and increase in CO, CO_2 and tar production with regenerated catalysts was probably partly due to the effect of the higher F/C ratio. Therefore, it can be estimated that there was only a slight decrease in the catalyst activity on regeneration.

Furthermore, it has been reported by other users of nickel catalysts that about 9% to 17% of the nickel content is lost during the regeneration of a nickel catalyst. The decrease in the nickel content of the catalyst may also contribute to the decrease in the activity of regenerated catalyst.

4.11 Hydrogasification of Pure Cellulose

Aromatic compounds of lignin in the wood have been claimed to be the major source of char production during the gasification process (Antal, 1985). To verify this behavior in the catalytic hydrogasification process, one experiment was carried out using a very low ash microcrystalline cellulose (PH-102, Avicel) as feed in place of wood. Following is the elemental analysis of the cellulose feed (also given in Section 3.5).

Element	% by weight (a)
Carbon	42.96
Hydrogen	6.3
Oxygen (by diff.)	50.74
Nitrogen	0.0
Ash	0.0

(a) Including 2.9% moisture

Average particle size 100 µm

This cellulose was gasified in the presence of the Lab (2) nickel catalyst at a temperature of 500°C. The gasification yields from this experiment are presented in Table 4.15 and are compared to the yields from an experiment with the wood at 500°C. Less than 1% of the cellulose feed converted to char whereas wood produced 12.44% char at the same reactor conditions. It can be concluded therefore that lignin and/or hemicellulose are the likely precursors for the char production. Since the tar and CH_4 yields are very similar for the wood and cellulose, it is likely that the cellulose in the wood is the primary source of the methane produced, most probably through the methanation of CO on the nickel catalyst.

Table 4.15

HYDROGASIFICATION OF WOOD VS. CELLULOSE
Lab(2) Ni Catalyst, 17% Ni, 500°C, 0.44 s

RUN NO.	G-14	G-17
Feed Material	Wood	Cellulose
Feed Particle, um	105-250	100
F/C RATIO, l/hr	1.45	0.95
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)		
CO	2.10	4.33
CO_2	1.89	2.14
CH_4	43.71	46.21
C_2 +	0.18	0.66
Total Gas	47.87	53.33
Char	12.44	0.92
Tar	4.78	5.04
Water	46.45	45.91
TOTAL YIELD	111.54	105.20
TOTAL REFORMABLE GASES	45.98	51.19
TOTAL GAS CARBON	70.82	77.61
CARBON IN CH_4	67.60	71.46
REFORMABLE C IN GAS	98 %	98 %
SELECTIVITY FOR CH_4	95 %	92 %

4.12 Hydrogasification of Char

In place of wood, char was fed in the reactor for an experiment at 550°C. This experiment was carried out to study the origin of char during catalytic hydrogasification of wood. It has been reported by Shafizadeh (1982) that some part of the wood directly forms char in the pyrolysis process, which is called primary char. Secondary char is formed due to cracking of organic liquids (tar) during the gasification process. The char feed for this experiment was obtained from a wood pyrolysis pilot plant operating at the University of Waterloo, and is considered to be a mostly primary char. This char was formed in the pilot plant during Run P-59 using IEA poplar wood feed at 550°C, resulting in 9.34% of wood converted to char during pyrolysis in a fluidized bed of sand particles. During catalytic hydrogasification of wood at the same temperature and residence time, about 10.7% char was formed. However, only 16.38% of the char feed, according to the results given in Table 4.16, could be converted to gases by catalytic hydrogasification. Assuming that the primary char cannot be further gasified at 550°C, and only secondary tar reacts, the amount of secondary char formed in a hydrogasification reaction at 550°C may be estimated as follows:

Table 4.16

Hydrogasification of Char

Run No.	G-42	G-28	G-29
Feed	poplar wood	poplar wood	char
Bed	sand	Lab (3) Ni catalyst	Lab (3) Ni catalyst
Temperature, °C	550	550	550
Yields (wt % of feed, mf)			
Char	9.34	10.70	67.36 (Unreacted)
Water	14.91	39.81	17.01
Tar	51.87	0.98	-
Gases	23.52	55.99	16.38

Primary char = 9.34 (1-0.164) = 7.81

Secondary char = (10.7-7.81)*100/10.7 = 27%

Assuming that the char formed during hydrogasification is from two sources, that is, primary char and secondary tar resulting from decomposition reactions of the tar, and assuming that the same proportion of primary char forms in straight pyrolysis or hydropyrolysis, then it appears that only about 27% of the char formed during the catalytic gasification is due to cracking of tar and the major fraction of char is formed due to the direct conversion of wood to char.

4.13 Hydrogasification with Ruthenium Catalyst

A ruthenium catalyst, named Lab (6) Ru, was prepared in the laboratory using alumina (Al-1404 T, Harshaw) as support; the same support that was used in the preparation of all nickel catalysts. The method of preparation of ruthenium catalyst is given in the Appendix. The ruthenium catalyst contained approximately 1.5% ruthenium. Two experiments were carried out using Lab (6) Ru catalyst at temperatures of 500°C and 550°C. The yields of products from these experiments are compared in Table 4.17 with the yields from experiments using two different nickel catalysts (containing 3% nickel and 8.8% nickel) at 550°C. With the ruthenium

Table 4.17

HYDROGASIFICATION OF RUTHENIUM CATALYST
AND COMPARISON WITH NICKEL CATALYSTS

RUN NO.	G-39	G-40	G-37	G-50
Catalyst description	Lab(6)Ru	Lab(6)Ru	Lab(4)Ni	Lab(3)Ni
Catalyst Metal %	1.5	1.5	3.0	8.8
Temperature, °C	500	550	550	550
Residence Time, sec	0.51	0.48	0.44	0.44
F/C RATIO, l/hr	3.69	3.59	3.27	3.68
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)				
CO	14.53	21.38	20.20	15.84
CO_2	10.44	11.75	10.23	12.95
CH_4	3.22	5.01	4.09	11.96
C_2H_4	0.39	0.56	0.50	0.27
C_2H_6	0.62	0.42	0.36	0.24
C_3	0.45	0.64	0.69	0.38
C_4^+	1.57	2.23	3.95	2.05
Total Gas	31.21	41.99	40.03	43.68
Char	17.58	15.45	16.81	13.88
Tar	26.50	21.21	17.15	18.40
Water	20.45	19.93	24.05	20.26
TOTAL YIELD	95.73	98.57	98.04	96.21
REFORMABLE GASES	20.77	30.24	29.80	30.73
TOTAL GAS CARBON	28.82	39.81	39.33	44.77
CARBON IN CH_4	4.98	7.74	6.33	18.49
REFORMABLE C IN GAS	80 %	83 %	85 %	84 %
SELECTIVITY FOR CH_4	17 %	19 %	16 %	41 %

catalyst, the production of CO, CO_2 and CH_4 increased and production of char, tar and water decreased with the increase in temperature.

Comparing the yield of gasification products using ruthenium catalyst and using two different nickel catalysts at 550°C and about the same F/C ratio, the amount of gasification products obtained using ruthenium catalyst can be compared very well with the nickel catalyst containing only 3% nickel. The performance of Lab (3) Ni catalyst, containing 8.8% nickel, was better than ruthenium catalyst in respect of selectivity for CH_4 production and the total gas production. At 550°C, the selectivity for CH_4 was 41% with 8.8% nickel catalyst compared to only 19% with ruthenium catalyst. The ruthenium catalyst is very expensive compared to the nickel catalyst. Therefore, although the ruthenium catalyst shows good activity, it cannot be judged to be better than nickel catalyst containing a minimum of 8.8% nickel for wood gasification. Although the ruthenium content was low at 1.5%, most commercial ruthenium catalysts contain only about 20% as much active metal as do nickel catalysts, and so the comparison made here is a reasonable one. However, further limited tests with catalyst containing about 5% ruthenium would probably be warranted.

4.14 Hydrogasification with Cobalt-Molybdenum Catalyst

The yields of gasification products from the two experiments which were done using a commercial cobalt-molybdenum catalyst were compared with the yields obtained using a nickel catalyst at 450°C and 550°C. The details of the cobalt-molybdenum catalyst are given below.

Cobalt-Molybdenum Catalyst -

Manufacturer	Harshaw Catalysts
Catalog No.	CoMo-0603 T 1/8"
Surface area (a):	166 m^3/g
Pore Volume (a)	0.40 cc/g
CoO	3%
MoO	12%

(a) These properties are for the particular form and size of the catalyst as received from the industry. This catalyst was crushed to a required size range and then used for experiments.

Gasification yields using a cobalt-molybdenum catalyst and a nickel catalyst at 450°C and at 550°C are compared in Table 4.18. The production of CO and CO_2 was higher and the production of CH_4 was lower with Co-Mo

Table 4.18

Comparison of gasification yields with a cobalt-molybdenum catalyst and a nickel catalyst

Run No.	G-25	G-15	G-24	(a)
Catalyst	Co-Mo	Ni	Co-Mo	Ni
Temperature, °C	450	450	550	550
Resi. Time, s	0.46	0.45	0.44	
TOTAL YIELD OF COMPONENTS (WT. % OF FEED, mf)				
CO	8.69	1.86	13.33	5
CO2	11.88	1.71	11.85	4
CH4	1.73	35.21	4.62	45
C2H4	0.47	Traces	1.66	Traces
C2H6	0.35	Traces	0.90	Traces
C3	0.71	Traces	0.69	Traces
C4+	6.77	Traces	5.02	Traces
Total gas	30.59	39.01	38.06	53
Total gas carbon	32.22	59.36	41.04	80
Char	21.9	14.08	18.33	10
Tar	27.08	14.3	8.34	4
Water	24.8	36.0	30.71	42
Selectivity for CH4	9 %	95 %	18 %	93 %
Reformable C in gas	79 %	98 %	83 %	97 %

(a) These values were obtained using Figure (4.1) to Figure (4.4).

catalyst compared to nickel catalyst. The production of char and tar was 30% to 50% lower and the gas production (and gas carbon content) was 30% to 50% higher with nickel catalyst than with Co-Mo catalyst. However, the production of higher hydrocarbon gases (C_2H_4, C_2H_6 etc.) was higher with Co-Mo catalyst whereas, nickel catalyst produced only traces of these gases. The nickel catalyst appears to have stronger cracking activity than the cobalt-molybdenum catalyst and the nickel catalyst is, particularly, more suitable for selective methane production.

4.15 Gasification with ($CO + H_2$) Gas Mixture

A 50% CO and 50% H_2 gas mixture was used to study the possibility of recycling a fraction of the product gas from the hydrogasification process back into the reactor. In one experiment, no wood was fed but only the CO/H_2 gas mixture was fed in the reactor, which contained Lab (3) nickel catalyst at 550°C. This was done to study the activity of the catalyst towards a CO/H_2 mixture at reaction conditions. The products of this experiment are given in Table 4.19. Of the hydrogen fed, 67.6% converted to CH_4 and 21.56% remained unreacted. Only 4.85% of the hydrogen was associated with the water product. An equilibrium calculation showed that the actual yield of CO was 137%, CO_2 88%, CH_4 79%,

Table 4.19

GASIFICATION WITH 50% CO AND 50% H_2 GAS MIXTURE
Lab(3) Ni catalyst, 8.8% Ni, 550°C, 0.44 s

RUN NO.	G-53	G-56	
F/C Ratio, l/hr	3.31	4.61	
Total wood fed, g	NIL	29.13	
Total CO/H_2 gas fed, g	138.09	137.23	
TOTAL YIELD OF COMPONENTS		(I)*	(II)*
CO	19.16	37.95	224.44
CO_2	51.15	35.05	207.26
CH_4	17.99	11.89	70.34
C_2 +	0.04	0.16	1.02
H_2	1.45	2.77	16.41
Total Gas	89.78	87.83	519.46
Char	0.47	5.09	30.12
Tar	0.00	0.34	2.00
Water	2.93	4.84	28.61
TOTAL YIELD	93.17	98.10	580.19
TOTAL REFORMABLE GASES	38.63	52.81	312.19
TOTAL GAS CARBON	89.24	84.21	425.39
CARBON IN CH_4	33.74	21.53	108.78
HYDROGEN IN CH_4	67.60	45.32	287.79
HYDROGEN AS H_2 IN GAS	21.56	41.97	266.50
HYDROGEN IN WATER	4.85	8.13	51.63
REFORMABLE C IN GAS	61 %	73 %	73 %
SELECTIVITY FOR CH_4	38 %	26 %	26 %

* The yields of products for Run G-56 is defined in two columns :
(I) On the basis of CO/H_2 gas mixture plus wood (mf) fed.
(II) On the basis of only wood (mf) fed.

H_2O 153% and H_2 185% of the equilibrium value. Apparently, neither the methanation of CO to form CH_4, nor the reaction of CO and H_2O to form CO_2 proceed rapidly enough to attain equilibrium at the conditions used, although the equilibrium of the water gas reaction is the more closely approached.

One experiment was also done using the CO/H_2 gas mixture with wood. The products from this experiment are also presented in Table 4.19 on two different bases, (i) the weight % of total CO/H_2 gas mixture plus moisture free wood fed and (ii) the weight % of only moisture free wood fed. This was done to determine the conversion of wood to char and tar because there was essentially no char or tar production with only CO/H_2 gas mixture. As seen in Table 4.19, on the basis of moisture free wood fed, 30.12% of the wood converted to char and 2.0% converted to tar. During the gasification of wood with only H_2 gas with the same catalyst and reactor conditions, about 10% of the wood converted to char. Therefore, the high yield of char during this experiment may be due to the effect of CO and H_2 partial pressures as well as the high F/C ratio during these experiments. For experiments with CO/H_2 gas mixture, the weight of CO/H_2 mixture consumed was more than the weight of wood fed and the CO in the gas

mixture also appeared to affect the activity of the catalyst. Therefore, the F/C ratio for these experiments was calculated using the total mass of wood and gas mixture consumed. On the basis of the total gas mixture and wood consumed, 37.95% CO and 2.80% H_2 was present in the product gas from the experiment with wood compared to only 19.16% CO and 1.45% H_2 from the experiment with CO/H_2 gas mixture only. The production of CH_4 was low and the production of char and water was higher with wood and gas feed compared to only gas feed. High production of CO_2 and low water yield during these experiments could also be explained by the high CO content of the gas mixture together with catalysis of the shift reaction as well as by the high F/C ratio during these experiments. At 550°C, the production of CO_2 is somewhat favored over CO by the water gas reaction equilibrium. High production of CO_2 reduces the carbon recovery to reformable gases but it may also have two favorable effects, (i) it consumes most of the undesired oxygen from the feed stock and (ii) it reduces the water production so more hydrogen is available for the methanation reaction.

Very high yields of CO_2 and char with a CO/H_2 gas mixture may indicate a deficiency of hydrogen on the catalyst surface during the gasification process. To

use product gases for recycling, it may be necessary to enrich the recycling gas with hydrogen which could be done by separating some hydrogen from the product gases by a diffusion process and then mixing it with the recycling gas stream. Further research is needed to establish optimum conditions for recycling the product gases.

4.16 Gasification with (CO_2 + H_2) Gas Mixture

A 33% CO_2 and 67% H_2 gas mixture was used for wood gasification in one experiment. The purpose of this experiment was to study the hydrogenation of CO_2 on the catalyst surface. It has been reported that CO_2 can gasify some of the char during gasification of wood. During this experiment the wood was gasified on Lab (3) Ni catalyst at 550°C in CO_2/H_2 atmosphere. As was done with CO/H_2 gas mixture, the products of this experiment are presented in Table 4.20 on two different bases (i) as the weight % of total CO_2/H_2 gas mixture plus moisture free wood and (ii) as the weight % of only moisture free wood.

On the basis of only moisture free wood, the conversion of wood to char was 9.13% and to tar was 5.82% at very high F/C ratio of 6.15. The production of char and tar was comparatively less with CO_2/H_2 gas mixture than

Table 4.20

GASIFICATION OF WOOD IN PRESENCE OF 33% CO_2 AND 67% H_2 GAS MIXTURE, Lab (3) Ni Cat., (8.8% Ni).

RUN NO.	G-58	
Temperature, °C	550	
Residence Time, s	0.44	
F/C Ratio, l/hr	6.15	
Total Wood Fed, g	49.98	
Total Gas Mixture Fed, g	131.37	
TOTAL YIELD OF COMPONENTS,	(i)*	(ii)*
CO	42.69	11.41
CO_2	176.47	47.16
CH_4	34.92	9.33
C_2 +	0.34	0.10
Total Gas	254.42	68.00
Char	9.13	2.44
Tar	5.82	1.56
Water	61.43	16.42
TOTAL YIELD	330.80	88.41
REFORMABLE C IN GAS	48 %	48 %
SELECTIVITY FOR CH_4	28 %	28 %

* The yield of products of experiment with CO_2/H_2 gas mixture are defined in two columns -

(i) On the basis of only moisture free wood fed.

(ii) On the basis of total gas mixture and moisture free wood fed.

with H_2 alone. For a typical experiment at high F/C ratio (more than 3.5), about 13% char and 16% tar production was obtained under H_2 atmosphere. The production of char was lower with the CO_2/H_2 gas mixture than with the CO/H_2 gas mixture, 9.13% vs. 30.12%, suggesting that CO_2 is capable of gasifying char on the catalyst surface and increasing the cracking activity of the catalyst. The hydrogen partial pressure was greater during gasification of wood with CO_2/H_2 than with CO/H_2. Even then, the yield of CH_4 (9.33%) was lower than the yield of CH_4 (11.89%) with CO/H_2 gas mixture indicating that some of the CH_4 production was probably via CO methanation.

$$CO_2 + H_2 \text{ ==== } CO + H_2O$$

$$CO + 3\ H_2 \text{ ==== } CH_4 + H_2O$$

CO_2 in the gaseous products is most probably underestimated for this experiment, because it was difficult to maintain a constant flow rate of CO_2 gas. The total yield of products was only 88.4% on the basis of total gas and wood (mf) fed.

It appears that in the presence of CO_2 more char is gasified and, therefore, the catalyst would retain its activity for a longer period. Hence, during the recycling of product gas mixture into the reactor, the

presence of CO_2 could act to reduce the char production and increase the catalyst lifetime. Further investigation of this behaviour is required.

4.17 Tests of Miscellaneous Commercial Catalysts

Three additional catalysts were received from industry and were used to study their suitability for the gasification of wood. Manufacturer's specifications for these catalysts are given in Figure 4.10.

One nickel catalyst (C11-9-02) was received from United Catalysts Inc. This catalyst contained 12% nickel on a ceramic support. Run G-33, shown in Table 4.21, was carried out at 550°C using this catalyst. As this catalyst is basically a steam reforming catalyst, a high production of CO (30.21%) was obtained but the production of CH_4 and CO_2 was close to 9% each. The production of water was only about 16% because of the low level of methanation activity. This favorably reduced the consumption of hydrogen by the undesired formation of water. The char production (9.63%) was not very different from the yield obtained at 550°C with the catalysts prepared in this laboratory. The tar production of 18.58% was very high which may indicate that this catalyst may not have been tested at its optimal process conditions.

Figure 4.10

Ni-3266 E, 1/16", NICKEL CATALYST

Manufacturer Harshaw Chemical Company

A 50% nickel catalyst in extruded form, Physically rugged with an open pore structure and a low bulk density. Ideally suited for diffusion controlled reactions.

Support	Proprietary silica-alumina
ABD*	49 lbs./cu.ft.
Strength	15 lbs.
Surface Area	150 m^2/g
Pore Volume	0.50 cc/g

Ni-0901 S 1", NICKEL CATALYST

Manufacturer Harshaw Chemical Company

Contains 7.5% nickel oxide on alumina silica spheres. Used for the reforming of low molecular weight hydrocarbons, and ammonia decomposition.

ABD*	75 lbs./cu.ft.
Surface Area	1 m^2/g
Pore Volume	0.075 cc/g (approx.)

---

* ABD - Packed Apparent Bulk Density

Figure 4.10 (cont'd)

G-65 NICKEL CATALYST

Manufacture United Catalysts Inc.

G-65 nickel catalyst is the unreduced form of G-65RS catalyst. It contains 25% nickel on refractory support. This catalyst is used for the same processes as is catalyst G-65RS.

C11-9-02 NICKEL CATALYST

Manufacture United Catalysts Inc.

C11-09-02 catalyst contains 12% nickel on a ceramic support. This catalyst is able to withstand severe process conditions experienced during high pressure oxo, ammonia, hydrogen, and methanol synthesis, as well as those of reducing gas reformers for metallurgical applications. This high density nickel catalyst coupled with high stability of the carrier, provides excellent initial activity and a minimal rate of activity decline. C11-09-02 nickel catalyst operates between 593° and 1200° C up to a pressure of 44 atm.

Table 4.21

WOOD GASIFICATION WITH INDUSTRIAL CATALYSTS

RUN NO.	G-33	G-34	G-35
Catalyst description	C11-9-02 United	Ni-3266 Harshaw	Ni-0901 Harshaw
Catalyst Ni %	12.00	50.00	7.5 % NiO
Temperature, °C	550.00	550.00	550.00
Residence Time, s	0.44	0.44	0.42
Total Feed, g	17.78	96.07	49.31
Feed Particle, um	105-250	105-250	105-250
Moisture %	2.72	2.72	2.72
Catalyst Wt., g	50.53	48.53	50.90
Catalyst Particle,um	250-590	250-590	250-590
Total Run Time, min	30.00	30.00	22.00
MHSV, 1/hr	0.70	3.90	2.60
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)			
CO	30.21	12.94	12.35
CO_2	9.36	17.17	7.64
CH_4	9.29	27.69	1.77
C_2H_4	0.62	0.09	0.59
C_2H_6	0.39	0.03	0.19
C_3	0.85	0.07	0.41
C_4+	0.69	0.33	1.25
Total Gas	51.41	58.32	24.21
Char	9.63	7.96	10.43
Tar	18.58	10.36	54.12
Water	15.95	20.85	11.39
TOTAL YIELD	95.56	97.49	100.15
REFORMABLE GASES	42.05	41.15	16.57
TOTAL GAS CARBON	51.64	66.04	22.57
CARBON IN CH_4	14.64	43.64	2.79
SCM CH_4/FEED	0.14	0.42	0.03
REFORMABLE C IN GAS	90 %	85 %	81 %
SELECTIVITY FOR CH_4	28 %	66 %	12 %
HHV GAS/FEED	0.49	0.87	0.18

Two catalysts were obtained from Harshaw Chemical Co. The catalyst Ni-0901 contained 7.5% nickel oxide on alumina-silica support and it is normally used for reforming of low molecular weight hydrocarbons and for ammonia decomposition. Another Harshaw catalyst used was Ni-3266 nickel catalyst. This catalyst contained 50% nickel and it is claimed to be suited for diffusion controlled reactions.

Results of the experiments with all three industrial catalysts are presented in Table 4.21. The industrial catalysts were first crushed to the desired size fraction and then used for experiments.

Run G-35 was carried out using Ni-0901 nickel catalyst. As expected, CH_4 production was only 1.77% with this catalyst but a 12.35% yield of CO and 7.64% yield of CO_2 was obtained. The char production was about 10%, whereas a very high yield of 54.12% of tar was obtained suggesting that this catalyst did not have a good cracking or hydrogenating activity. Therefore, it is not suitable for gasification of wood.

The Ni-3266 nickel catalyst produced a very high yield of 58.32% of gases in Run G-34. The high production of gases may be due to the 50% nickel loading on the catalyst. CH_4 yield was only 27.69%, but 12.94% yield

of CO and 17.17% yield of CO_2 was obtained. The 10.36% uncracked tar is probably due to the very high feeding rate of wood (F/C ratio = 3.96) during this run - about twice the feeding rate for most other runs. The char yield of 7.96% was probably underestimated for this run as the total products yield was only 97.5% in spite of the fact that 165% H_2 (% wt. of hydrogen in wood fed) was consumed during this run. In view of the very high wood feed rate used, and the fact that feed rates over an F/C value of about 2.0 caused increased CO and CO_2 and tar yields (cf Section 4.7), the performance of the Harshaw Ni-3266 catalyst was promising, and further testing of this catalyst would be warranted.

4.18 Preliminary Tests of Catalyst Lifetimes

The lifetime of the laboratory-made type of nickel catalyst was studied in two ways. First, one experiment was allowed to run continuously for 135 minutes without refilling the wood feeder during this period. The second experiment was done in four cycles of 25 minutes each and after each cycle the wood feeder was removed and refilled close to its initial level. The purpose of this experiment was to determine the effect of operating time on the catalyst activity allowing for the effect of feed rate change as the feed hopper

became depleted. The feed rate of wood changed with the height of wood particles in the reactor, and a calibration had to be done to allow for this minor effect, inasmuch as a reduction in gas output at constant reactor conditions could be due to either a reduced feed rate of wood, or to a reduction in catalytic activity.

One experiment was carried out using Lab (3) Ni catalyst, at 550°C and at a vapor residence time of 0.44 s, and was stopped after the usual 30 minutes time. Another experiment was continued for 135 minutes using the same catalyst at the same reactor conditions as the previous experiment. This experiment had to be stopped because of the plugging of the product line between the reactor and the ice/water condensers. The F/C ratio was 1.56 l/hr for the 30 minutes long experiment and 1.15 l/hr for the 135 minutes long experiment. The results of these two experiments are compared in Table 4.22. The time-averaged yields of CO, CO_2 and char were lower and yields of CH_4 were higher in the long run than in the shorter run. The reason for this may be partly due to the lower F/C ratio for the long-time experiment, and this ratio decreased as the experiment progressed. The yield of tar increased from 0.48% in 30 minutes to 1.84% in 135 minutes. The feed rate was

Table 4.22

STUDY OF CATALYST LIFE-TIME

Lab(3) Ni Cat., 8.8% Ni, 550°C, 0.44 s

RUN NO.	G-31	G-49	G-54
Total Run Time, min	135.0	30.0	100.0 (4 @ 25 min)
F/C RATIO, l/hr	1.15	1.56	1.55
TOTAL YIELD OF COMPONENTS, (% WT. OF FEED, MF)			
CO	6.10	7.54	11.29
CO_2	5.02	6.74	9.35
CH_4	42.12	40.82	33.15
C_2H_4	0.04	0.05	0.09
C_2H_6	0.03	0.03	0.09
C_3	0.07	0.05	0.24
C_4^+	0.40	0.25	0.59
Total Gas	53.77	55.46	54.80
Char	8.62	11.31	9.81
Tar	1.84	0.48	6.95
Water	38.50	40.33	34.61
TOTAL YIELD	102.74	107.58	106.17
REFORMABLE GASES	48.75	48.72	45.45
TOTAL GAS CARBON	74.26	74.20	68.22
CARBON IN CH_4	65.14	63.13	51.26
REFORMABLE C IN GAS	96 %	95 %	92 %
SELECTIVITY FOR CH_4	88 %	85 %	75 %
HHV GAS/FEED	1.24	1.21	1.03

highest at the beginning of the long experiment but as the experiment continued, the feed rate decreased with time which would subsequently decrease the production of tar and increase the production of gaseous products. Water yield was probably underestimated for the 135 minutes long experiment. As the production of CH_4 was higher and the production CO and CO_2 was lower in 135 minutes than in 30 minutes, a higher yield of water was expected. These observations suggest that at low F/C ratio (1.15 l/hr) there was little if any decrease in the activity of nickel catalyst during 135 minutes of operation, since most of the differences in the two runs can be explained by the variation of feed rate with time.

Results of the experiment which was carried out for 30 minutes are also compared in Table 4.22 with another experiment (G-54) which was carried out in four cycles of 25 minutes each. During this experiment, the feeder was filled close to its initial level before starting the next cycle. Both these experiments (G-49 and G-54) were carried out at the same temperature, residence time and F/C ratio using the same Lab (3) Ni catalyst. The production of CH_4, water and char was lower and the production of tar, CO and CO_2 was higher in the 100 minute cyclic run than in the 30 minute run. Figure

4.11 shows the production of CH_4 and CO with time during the 100 minute time experiment in four cycles. Actual production of CH_4 and CO is shown by solid lines. The decrease in the production of CH_4 and CO during each cycle can be a compound effect of the decrease in feed rate and the decrease in catalyst activity. After each cycle when the feeder was refilled, the production of CH_4 and CO jumped to a peak initial value again. The production of CH_4 and CO was corrected for the change in the feed rate with time using the feeder calibration of feed rate vs. solids height, and the results are plotted as dotted lines on Figure 4.11 as an equivalent constant feed rate yield based on the initial feed rate. It is evident from this Figure that there was a moderate decrease in the catalyst activity with time in this experiment. The sudden decrease in the catalyst activity in the final cycle may be due to the inclusion of oxygen in the reactor. The reactor outlet line was opened for cleaning after completion of the third cycle and during this period some oxygen might have entered into the reactor, which in fact, could also have occurred as a result of periodic fillings of the feeder.

During the refilling of the feeder, air could enter the feeder and that feeder (now containing some oxygen) was

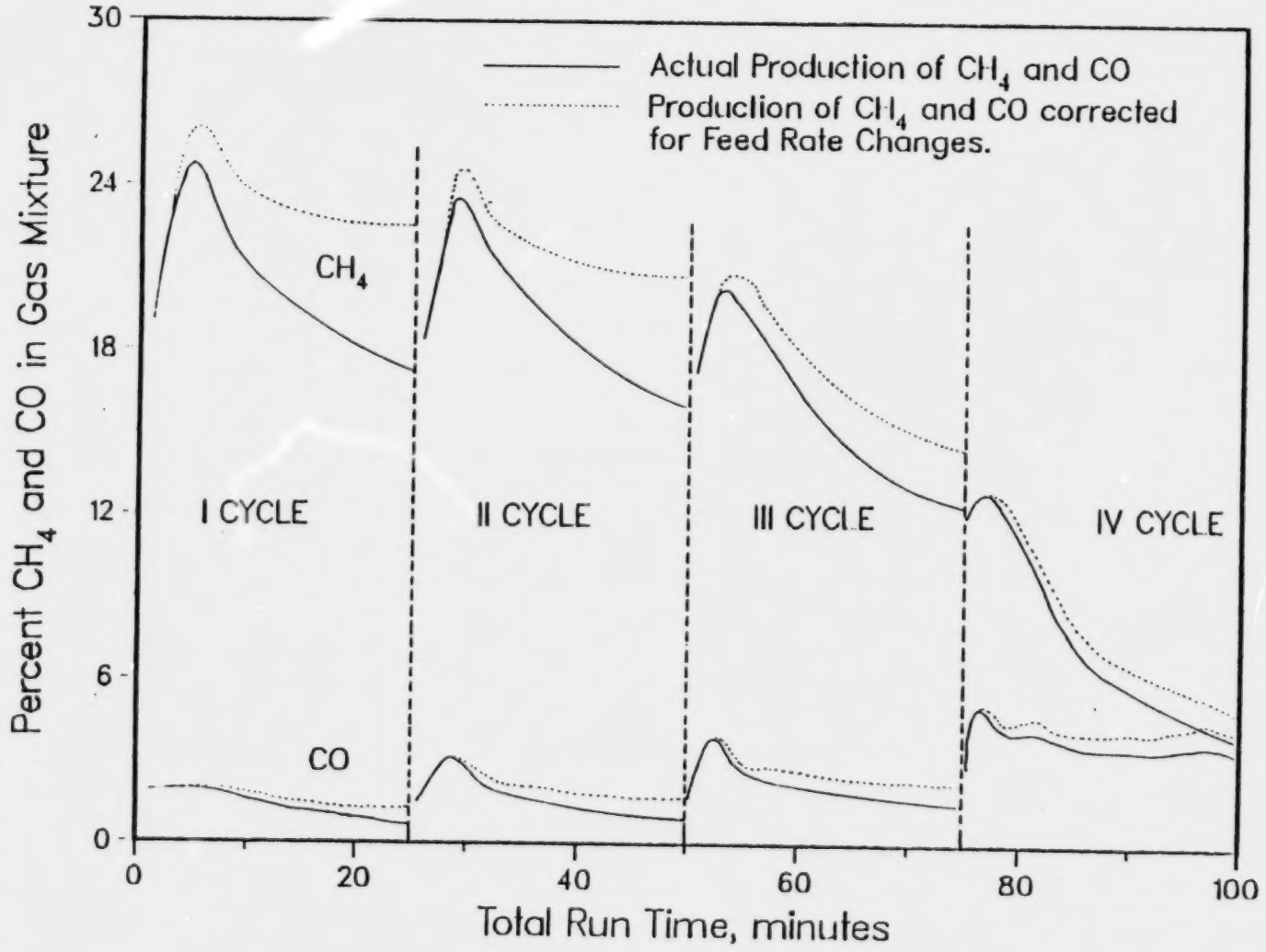


Figure 4.11 Yield of CH_4 and CO with Time
IEA Poplar Wood, H_2, Lab (3) Ni Catalyst, 550°C

used to feed the wood for the next cycle. Practically no decrease in the catalyst activity was observed when the feeder was not refilled during the experiment, which suggests that the oxygen in the feeder may also have been responsible for some decrease in the catalyst activity for the subsequent cycles.

On the basis of results of two longer experiments, it seems that there is little change in the catalyst activity at low F/C ratio (about 1.15 l/hr) but higher F/C ratio and the possible inclusion of oxygen in the reactor decreased the catalytic activity. Further research is needed to study the exact cause of change in the activity of nickel catalyst with time. The role of the secondary carbon deposition may be of importance, and special experiments to study this phenomena would be desirable. However, the run carried out for 135 min. (G-31) produced about 0.22 g char per g of catalyst, or a volume of char about twice the catalyst volume. Apparently this large char production had little effect on catalyst activity. If our estimate of 27% secondary char is accepted then a volume of secondary char equal to about half the catalyst volume would be formed. This amount of secondary char if formed on the catalytic surfaces and in the pores would be expected to cause a serious drop in catalyst

activity. The fact that this did not occur suggests that much of the secondary char may be physically removed by the action of the fluid bed and blown out of the reactor and the secondary char may itself be very porous and offer little resistance to diffusion at the catalytic surface. The physical nature of the secondary char deposit would need to be examined in special tests to investigate this latter speculation.

5. EQUILIBRIUM CALCULATIONS

5.1 Method

A calculation of the equilibrium production of the main gasification compounds was carried out by direct minimization of Gibb's function (Perry, 1984), assuming all gaseous products and water behaved ideally.

The equilibrium calculations were made using a computer program which would "burn" any feed for which composition was specified. A computer subroutine "OPTMUD", used to solve constrained optimization problems, was employed which is available in the subroutine library of the University of Waterloo mainframe computer. The value of Gibb's function was compiled from JANAF Tables of Thermodynamic Functions by interpolation.

In each calculation, the following were considered as possible products:

CO, CO_2, CH_4, H_2O, H_2

C_2H_4, C_2H_6, C_3H_6 and C_4H_{10}

No attempt was made to model "char" or "tar". For all conditions investigated, the only products present in significant amounts (with production rate of >0.0001 moles per hour) were CO, CO_2, CH_4, H_2O and H_2 under equilibrium conditions. It is important to note that

no hydrocarbon other than CH_4 is thermodynamically stable under gasification conditions. Ethylene, ethane and other higher hydrocarbons were produced in small amounts during most of the experiments in the present study, but these were non-equilibrium products.

The elemental composition (C, O and H) of all gaseous products including water was calculated from the experimental measurements and this composition was used in the computer program to determine the equilibrium production of the above five compounds. The predicted equilibrium production of each component was then compared with the actual production for each of these compounds.

The calculations were organized into two sets, in one of which the effect of temperature, and in the other of F/C ratio, on the equilibrium products, was studied. The results are presented in the form of plots.

5.2 Effect of Temperature

The equilibrium production of CO, CO_2, CH_4, H_2O and H_2 was calculated at different temperatures in the range of 400°C to 650°C. All the data used were from experiments carried out using Lab (2) Ni catalyst containing 17% Ni on alumina support. On comparison, it was found that all the gaseous hydrocarbons, other than CH_4, were

non-equilibrium products in the range of 400°C to 650°C.

The wood and hydrogen feed rates were different for different experiments. The F/C ratio varied between 1.18 l/hr to 1.83 l/hr during the six experiments carried out at different temperatures. Therefore, the production of all the compounds was plotted on two different bases:

5.2.1 As the percent of a compound in the product gas (assuming all the process water is in the gaseous phase). This plot represents the combined effect of temperature as well as of feed rate on the gasification products.

5.2.2 As the moles of a compound produced per atom of gas carbon or oxygen. The production of CH_4, CO and CO_2 was calculated on the basis per atom of gas carbon and the production of H_2O was calculated on the basis of per atom of oxygen. In this way, the relative production of each compound was represented independently.

Figure 5.1 to Figure 5.4 show the actual and equilibrium production of CO, CO_2, CH_4 and H_2O between 400°C to 650°C. One compound is shown in each Figure.

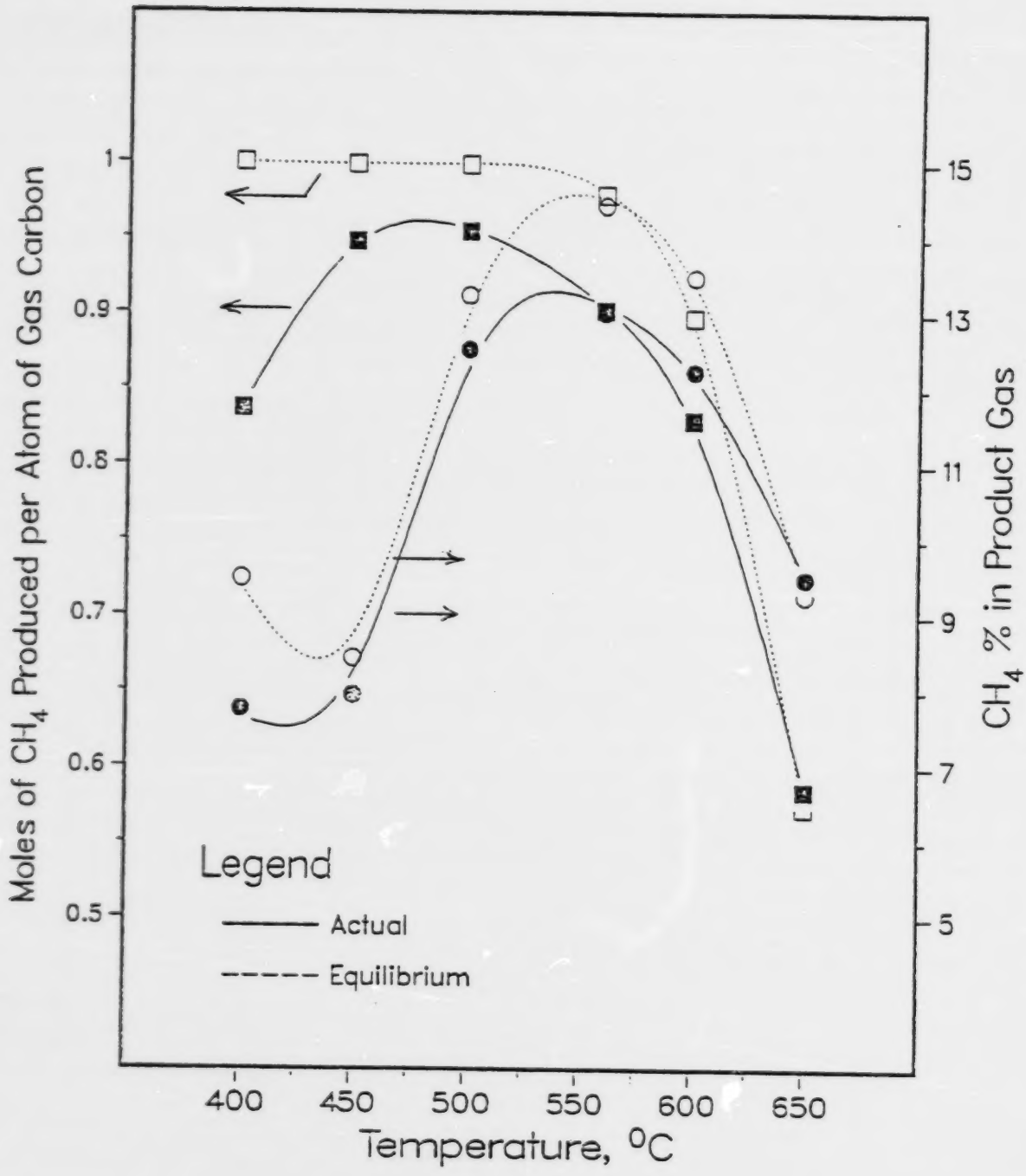


Figure 5.1 Effect of Temperature on Equilibrium and Actual Production of CH_4, Lab (2) Ni Catalyst, 0.44 s

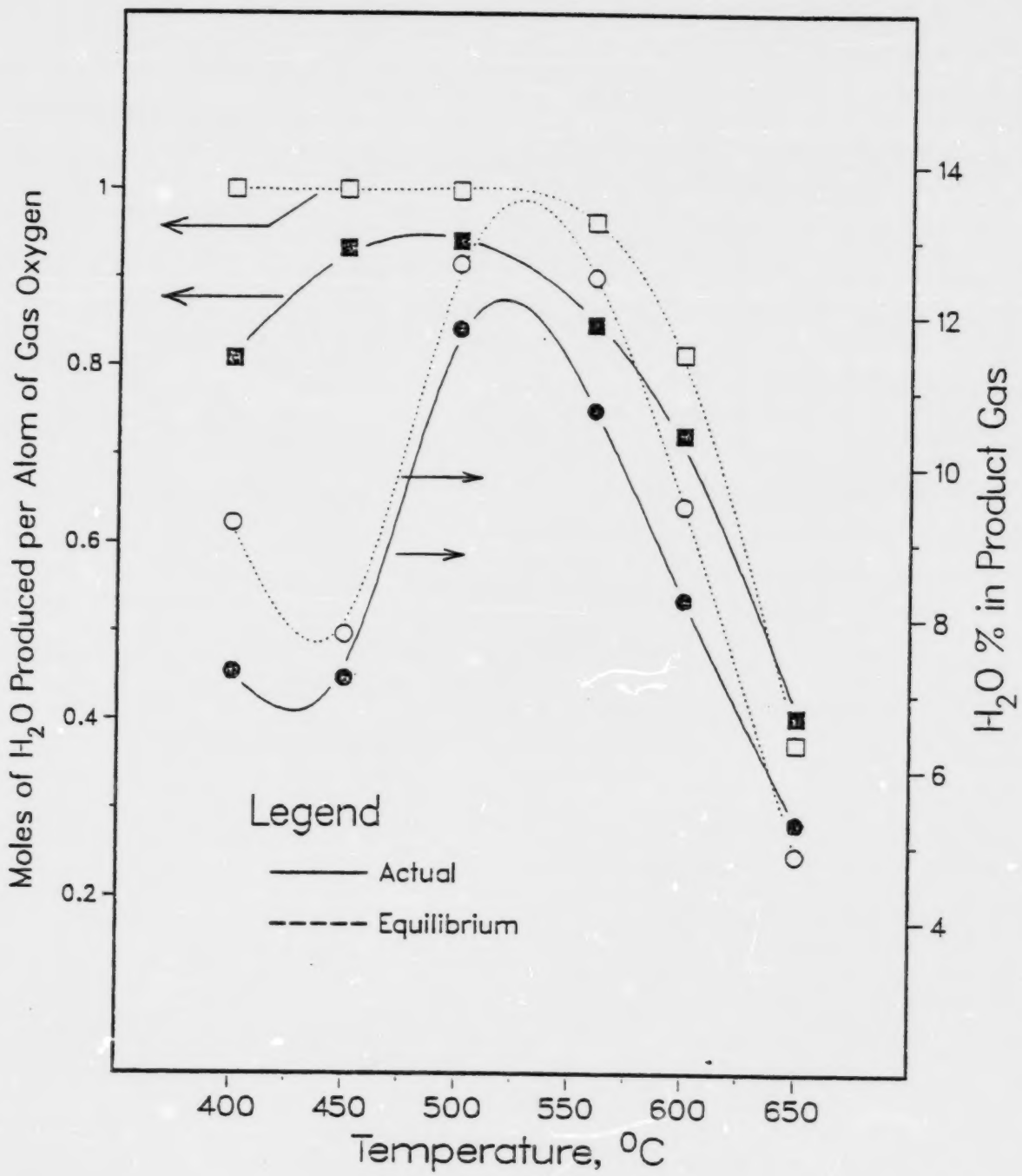


Figure 5.2 Effect of Temperature on Equilibrium and Actual Production of H_2O, Lab (2) Ni Catalyst, 0.44 s

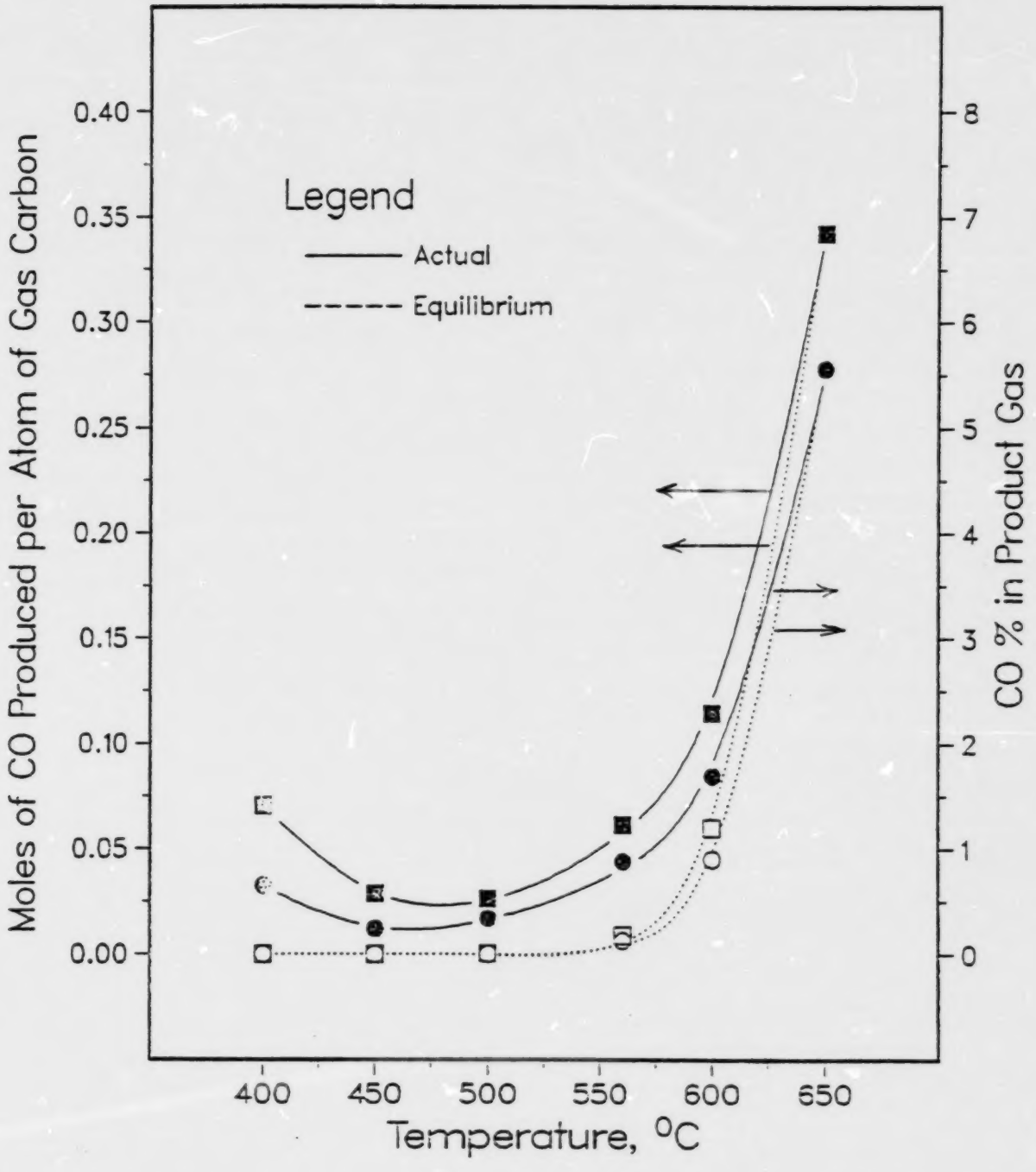


Figure 5.3 Effect of Temperature on Equilibrium and Actual Production of CO, Lab (2) Ni Catalyst, 0.44 s

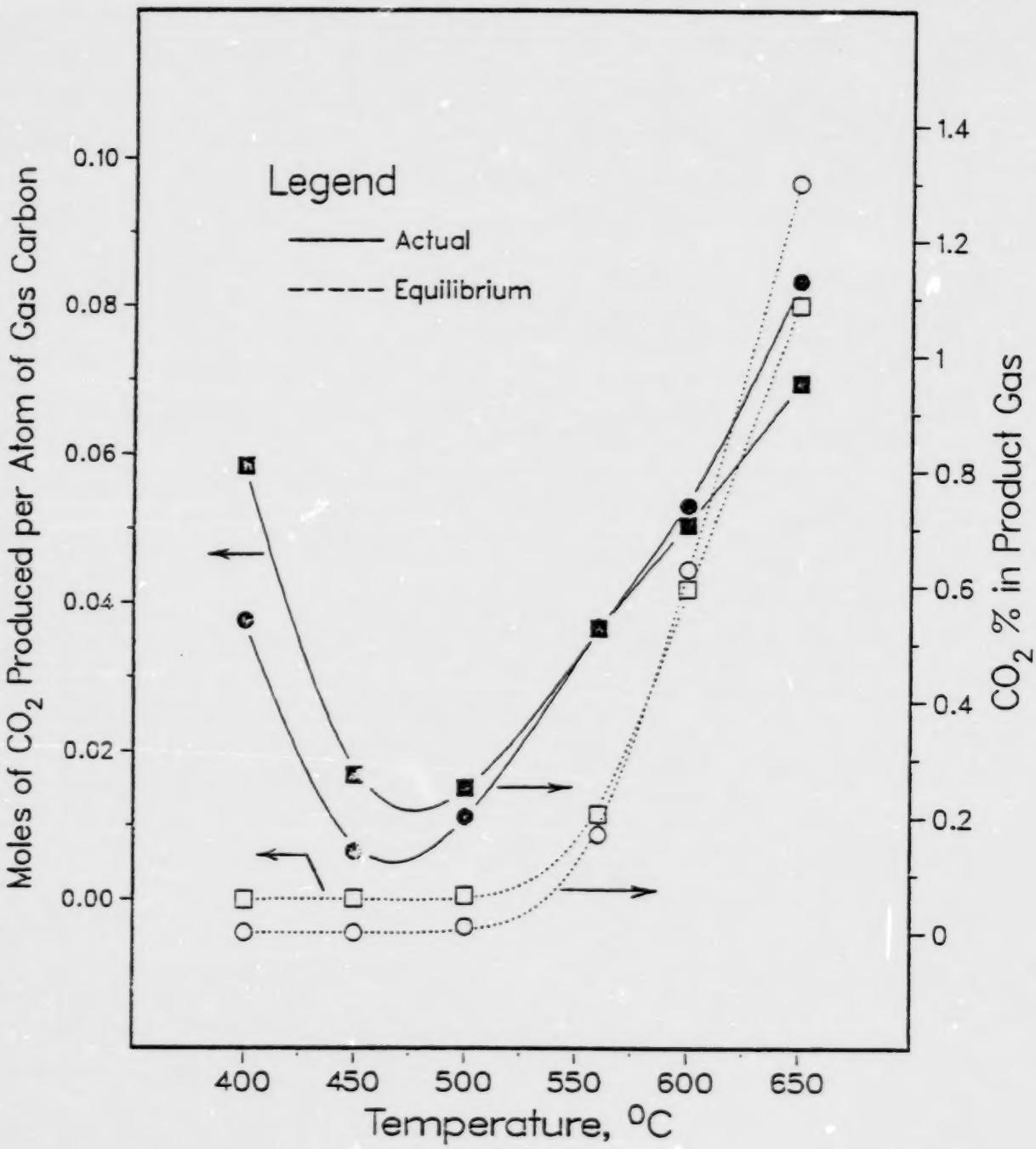


Figure 5.4 Effect of Temperature on Equilibrium and Actual Production of CO_2, Lab (2) Ni Catalyst, 0.44 s

On the basis of per atom of gas element (carbon or oxygen) present, the equilibrium curves show the almost total conversion of gas carbon to CH_4 and gas oxygen to H_2O below 500°C. At equilibrium, there is no production of CO and CO_2 below 500°C, but above this temperature, the production of CH_4 and H_2O starts decreasing and the production of CO and CO_2 starts increasing. At 650°C, the equilibrium production of CH_4 goes down to 0.57 moles/atom of gas carbon but the CO equilibrium production increases to 0.35 moles/atom of gas carbon and CO_2 equilibrium production increases to 0.08 moles/atom of gas carbon. The production profile of H_2O is very similar to that of CH_4. The actual production generally followed the same trend as the equilibrium production, except at 400°C where the F/C ratio was 1.83 l/hr, the highest among all these experiments, and a lower production of CH_4 and a higher production of CO and CO_2 was obtained at this temperature compared to their respective yields at 450°C.

The actual production of CH_4 and H_2O was always somewhat less than the predicted equilibrium production but CO and CO_2 showed the opposite trend. The maximum actual production of CH_4 was 0.95 moles/atom of gas carbon and of H_2O was 0.94 moles/atom of gas oxygen at 500°C, compared to the equilibrium maximum of nearly

unity for both. The minimum production of CO and CO_2 was 0.026 and 0.015 moles/atom of gas carbon respectively also at 500°C. The actual production of CH_4, H_2O, CO and CO_2 approached most closely to their equilibrium values at about 650°C.

On the basis of mole percent composition in the product gas mixture, the plots of CH_4, H_2O, CO and CO_2 show a combined effect of wood feed rate as well as temperature on their yields. As there was always a considerable excess of hydrogen during a gasification experiment, the shape of these plots was dependent upon the number of carbon or oxygen atoms present in the gaseous products. Hence, the difference between the actual production and the equilibrium production depicts the effect of feed rate on the production of different compounds as well as the effect of temperature.

As the production of CH_4 and H_2O followed the same pattern with temperature, it indicates that the CH_4 and H_2O production may have been largely due to the hydrogenation of CO:

$$CO + 3\ H_2 \quad ====== \quad CH_4 + H_2O$$

At lower temperatures (below 500°C), the production of CH_4 and H_2O was favored but above 500°C, the equilib-

rium shifted towards the left side and the amount of CO produced started to increase. The yield of CO_2 was also influenced by the presence of CO which seemed to be the major source of CO_2 production, probably via the water gas shift reaction:

$$CO + H_2O \quad ====== \quad CO_2 + H_2$$

If CO production was high (above 500°C), CO_2 production started increasing in parallel with CO. The rate of increase in CO production was almost 3 times that of CO_2, but at lower temperatures below 500°C, the rate of production increase of CO_2 was 1.4 times as much as that of CO. Therefore, below 500°C, the production of CO_2 was favored over the production of CO but above 500°C, CO production was favored. This behaviour agrees with the equilibrium of the water gas shift reaction which favors CO production at higher temperatures.

At low temperatures below 500°C, the gap between the equilibrium and actual production curves for these compounds increased, which indicates the reduced effect of the catalyst on reaction rates at lower temperatures. Above 500°C, the conversion of CO to CH_4 and CO_2 proceed rapidly but below 500°C, the methanation reaction is slower and not all the CO is converted to CH_4 at the reaction times and F/C ratios used.

5.3 Effect of F/C Ratio

To find out the effect of feed rate on the equilibrium and actual production of CH_4, CO, CO_2 and H_2O, the production of these compounds was calculated for four different F/C ratios at 550°C. All of the experimental data used were from tests carried out at 550°C using Lab (3) Ni catalyst containing 8.8% nickel on alumina. Here also, the production of CH_4, CO and CO_2 was calculated on the basis of per atom of gas carbon and the production of H_2O was calculated on the basis of per atom of gas oxygen. Figures 5.5 to 5.8 show the equilibrium and actual production of the four main gaseous products (assuming all the process water was in the gaseous form) at different F/C ratios. One compound is shown on each Figure.

The equilibrium curves predict that there is only a slight change in the production of any of these compounds with F/C ratio. At low F/C ratio, there is total conversion of gas carbon to CH_4 and gas oxygen to H_2O, and there is no production of CO and CO_2. As the F/C ratio is increased, the equilibrium production of CH_4 and H_2O decreases slightly and the production of CO and CO_2 correspondingly increases slightly. The reason for the changes in the equilibrium production of these

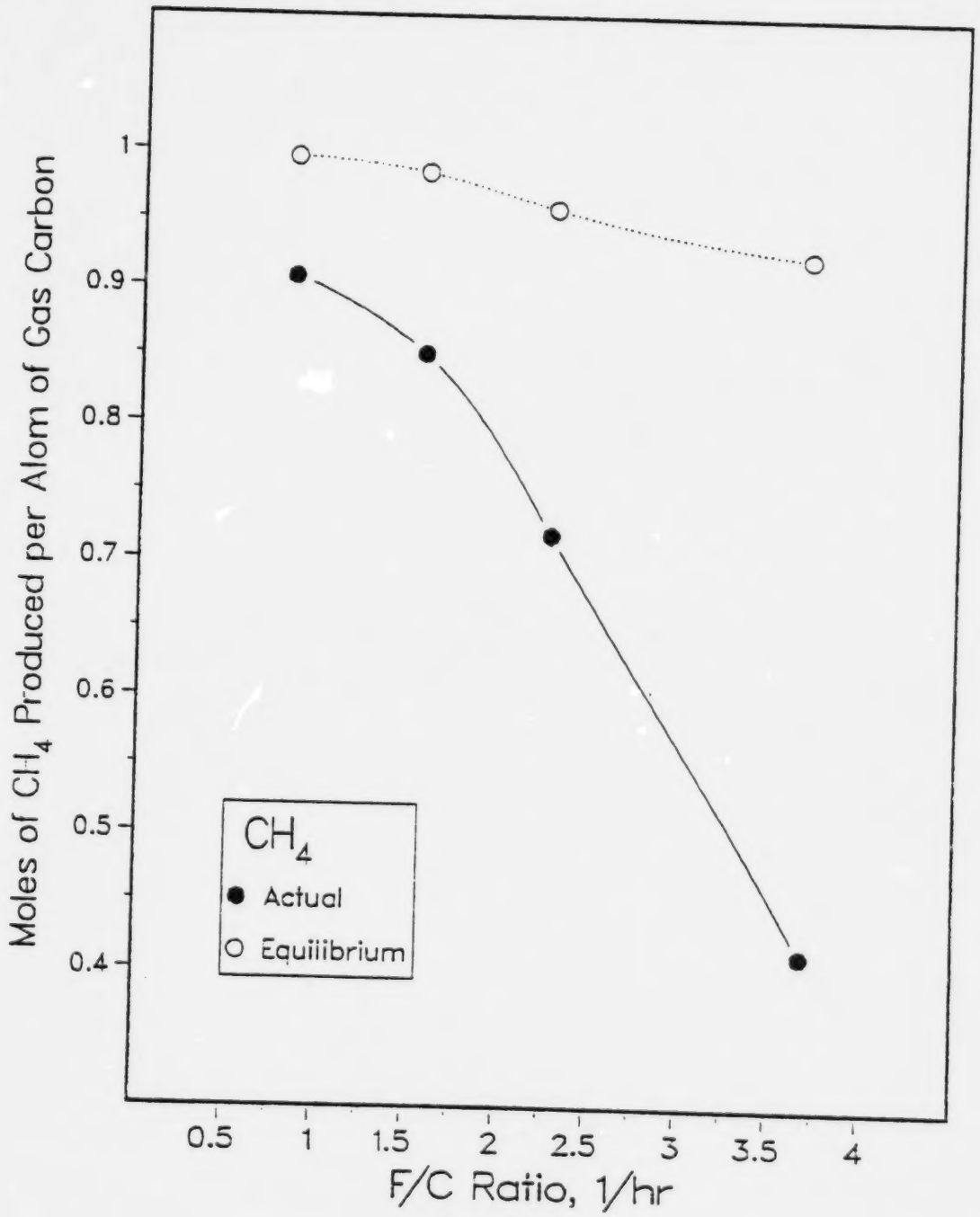


Figure 5.5 Effect of F/C Ratio on Equilibrium and Actual Production of CH_4, Lab (3) Ni Catalyst, 550°C

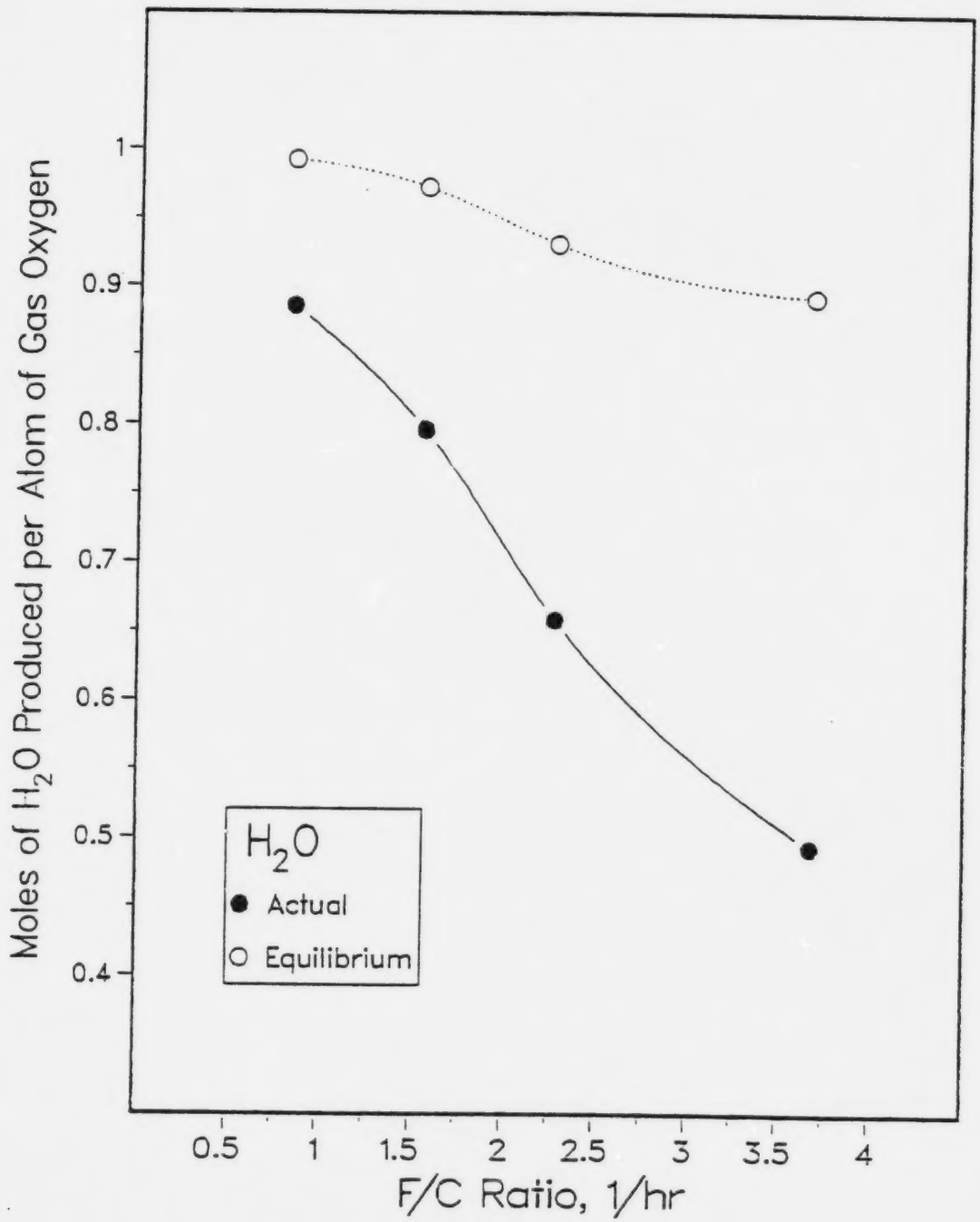


Figure 5.6 Effect of F/C Ratio on Equilibrium and Actual Production of H_2O, Lab (3) Ni Catalyst, 550°C

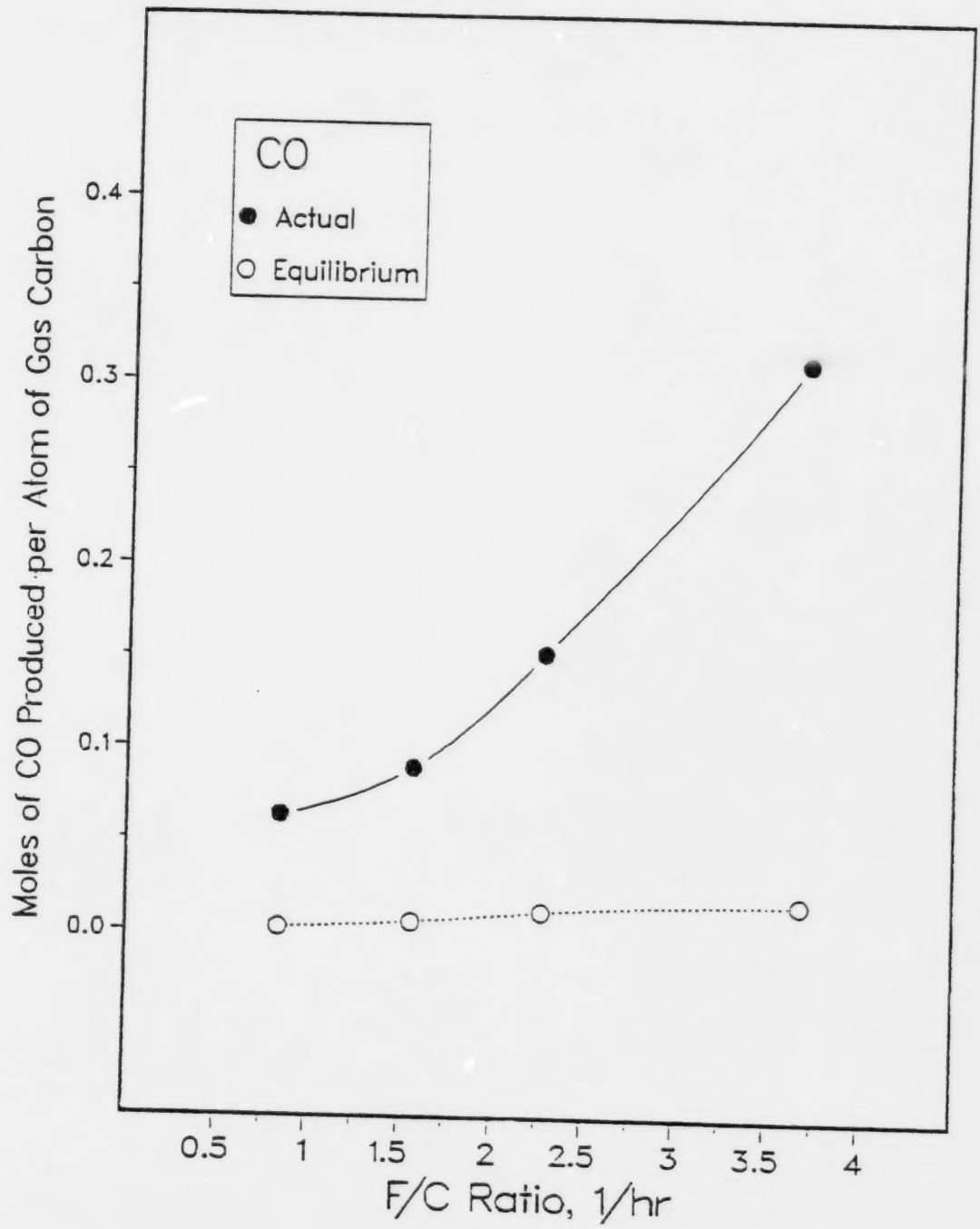


Figure 5.7 Effect of F/C Ratio on Equilibrium and Actual Production of CO, Lab (3) Ni Catalyst, 550°C

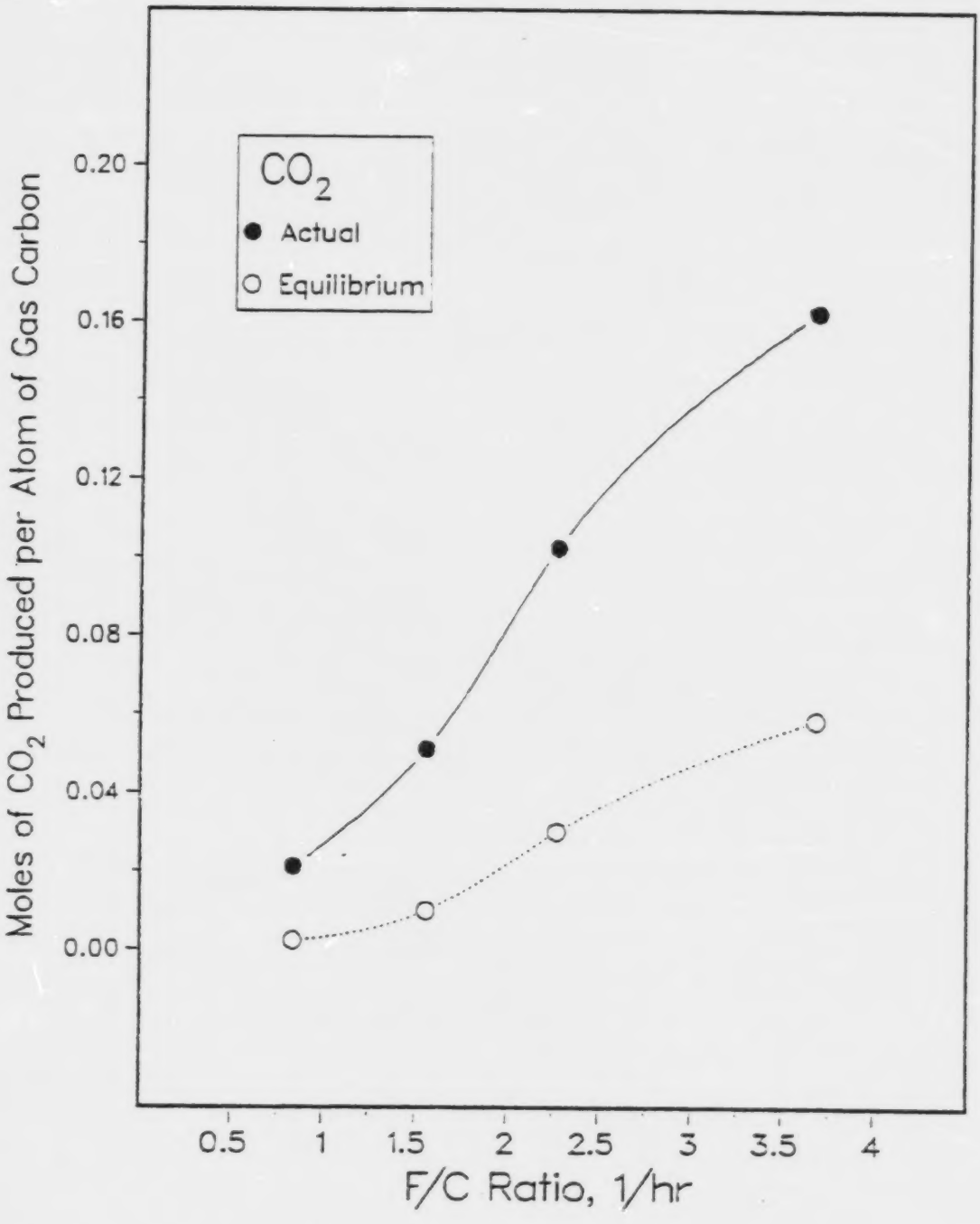


Figure 5.8 Effect of F/C Ratio on Equilibrium and Actual Production of CO_2, Lab (3) Ni Catalyst, 550°C

compounds is due to the change in hydrogen to carbon and hydrogen to oxygen ratios in the catalytic reactor as the F/C ratio varies with more or less the same hydrogen input rate but with a constant catalyst amount in the reactor.

Almost the same quantity of catalyst was used for all these experiments and only wood feed rate was changed to change the F/C ratio. Hence, these curves show the effect of feed rate on the actual production of gaseous compounds. The actual production of CO, CO_2, CH_4 (per atom of gas carbon) and H_2O (per atom of gas oxygen) at lowest and highest F/C ratio is shown in Table 5.1.

The production of CH_4 and H_2O decreased considerably and production of CO and CO_2 increased with the increase in F/C ratio. The total amount of gas carbon actually associated with CH_4, CO and CO_2 experimentally was always less than the total expected from equilibrium predictions (see Table 5.1). The rest of the carbon was consumed during the experiment by the production of gaseous hydrocarbons other than CH_4.

For all the compounds, the difference in the actual production and the equilibrium production increased with the increase in F/C ratio. As the feed rate was increased, it increased the amount of tar which had to

Table 5.1

Production per Atom of Gas Element (C or O)
at Different F/C Ratio
Lab (3) Ni Catalyst, 550°C

	F/C Ratio, 1/hr	
	0.84	3.68
Compound		
CH_4	0.9069	0.4130
H_2O	0.8858	0.4937
CO	0.0635	0.3127
CO_2	0.0211	0.1626

be cracked on the catalyst surface at the same reaction time, and at F/C ratio >1.5 l/hr, these conditions resulted in a considerable departure from equilibrium conditions.

5.4 Effect of Hydrogen-to-Feed Ratio

To calculate the effect of hydrogen partial pressure, the equilibrium production of CH_4, CO, CO_2 and H_2O was calculated at 550°C on the basis of hydrogen flow rate per hour per atom of the wood elements (carbon or oxygen). Two new ratios are defined to discuss the effect of hydrogen partial pressure:

5.4.1 H/C ratio is defined as the flow rate of hydrogen per hour per atom of wood carbon fed per hour.*

* Note that the C in the H/C ratio represents carbon, whereas the C in F/C ratio represents catalyst.

5.4.2 H/O ratio is defined as the flow rate of hydrogen per hour per atom of wood oxygen fed per hour.

The equilibrium production of CO, CO_2, CH_4 and H_2O is compared with their actual production at different H/C and H/O ratio in Figures 5.9 to 5.12. The actual production was taken from the results of the experi-

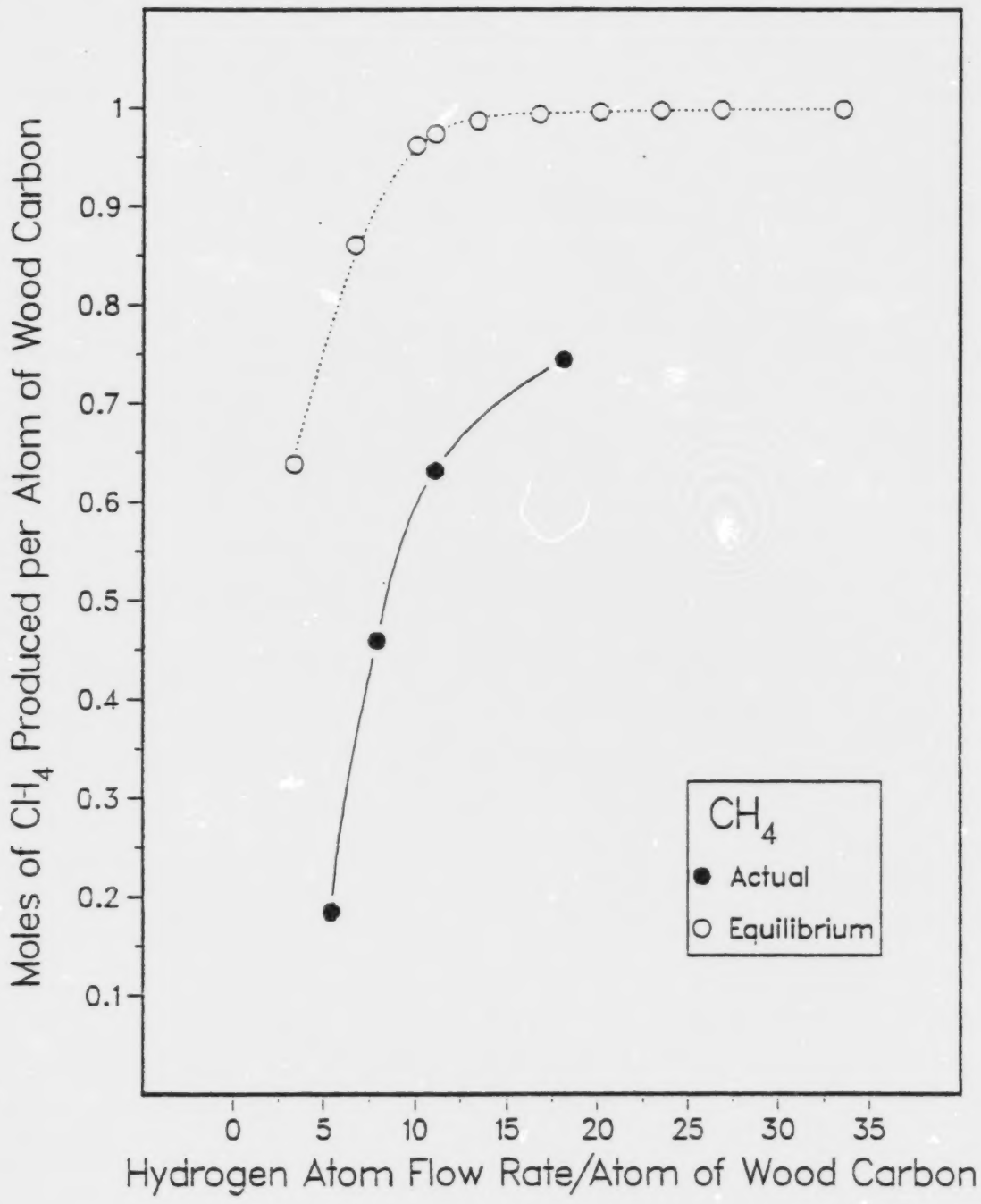


Figure 5.9 Effect of H_2 Partial Pressure on Equilibrium and Actual Production of CH_4, 550°C

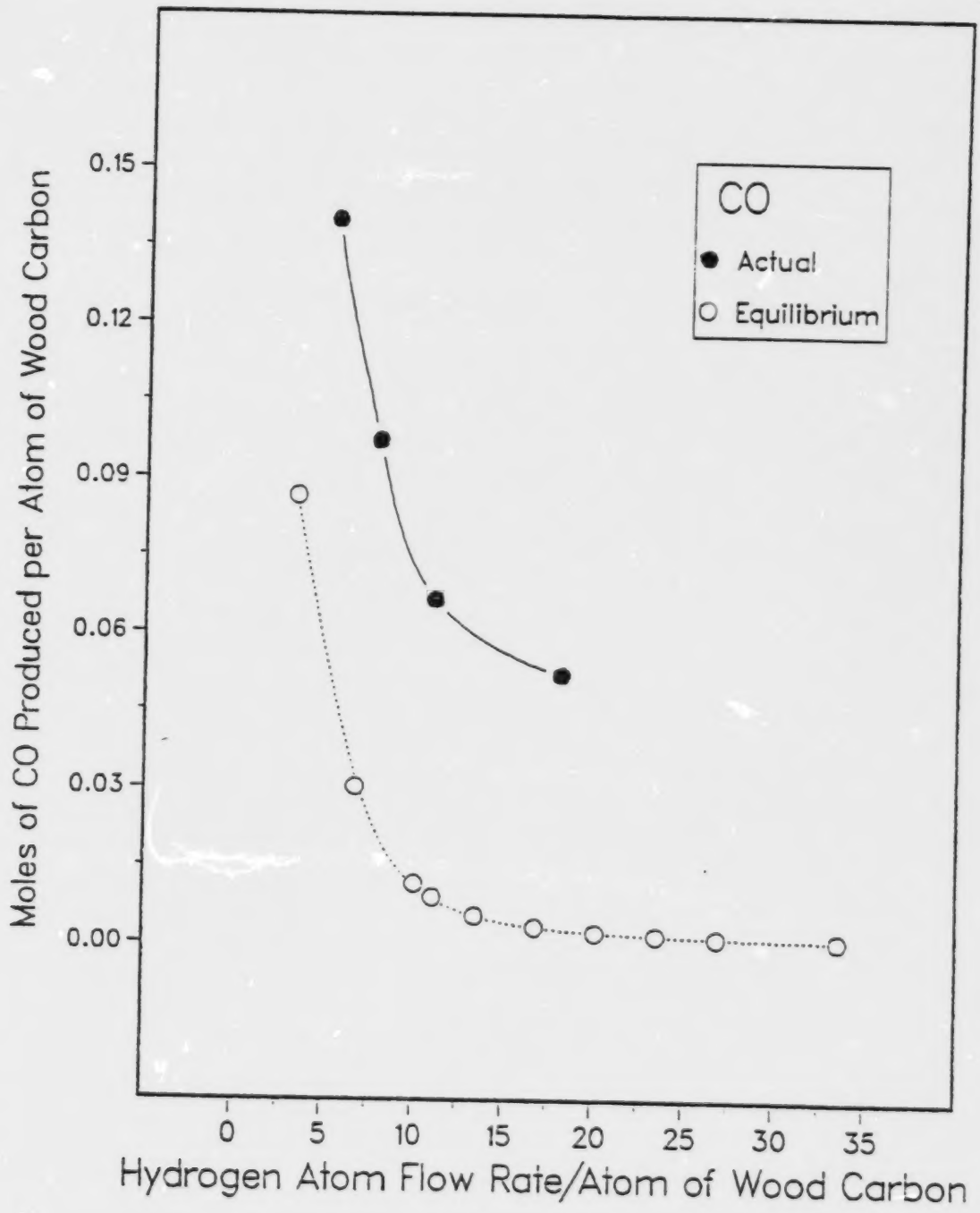


Figure 5.10 Effect of H_2 Partial Pressure on Equilibrium and Actual Production of CO, 550°C

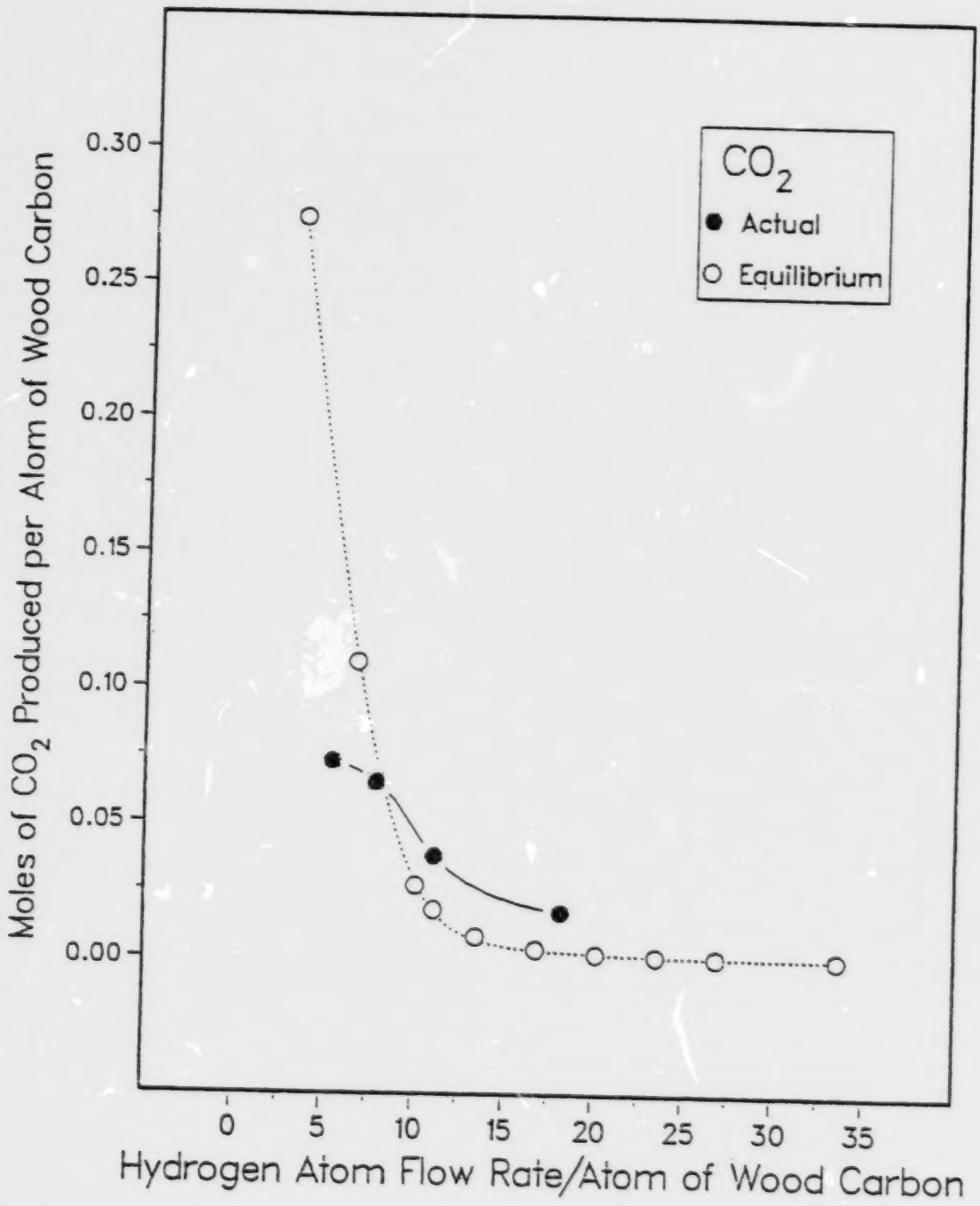


Figure 5.11 Effect of H_2 Partial Pressure on Equilibrium and Actual Production of CO_2, 550°C

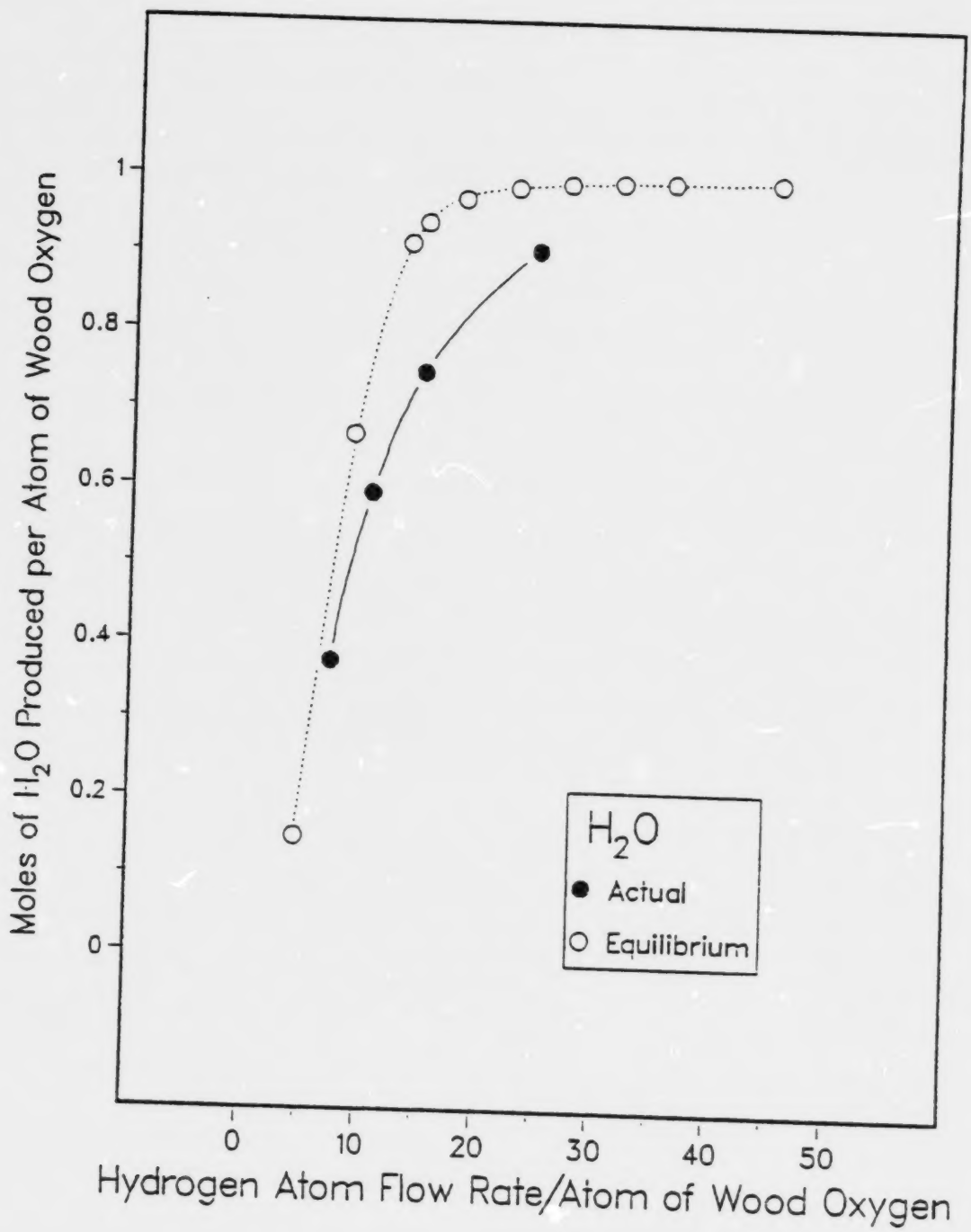


Figure 5.12 Effect of H_2 Partial Pressure on Equilibrium and Actual Production of H_2O, 550°C

ments which were carried out at different F/C ratios. The hydrogen flow rate was about the same during all these experiments and only wood feed rate was changed. So, as the F/C ratio was increased by increasing the wood feed rate, the H/C ratio and H/O ratios can be changed independently, but in the present study, the F/C ratio is inversely proportional to the H/C or H/O ratio. By changing the amount of catalyst in the reactor, the F/C ratio can be changed without affecting the H/C or H/O ratio.

As shown in Figure 5.9, the equilibrium production of CH_4 increased with increase in H/C ratio and all of the wood carbon converted to CH_4 above an H/C ratio of 12.5. The actual production of CH_4 also increased with the increase in H/C ratio. The maximum actual production of CH_4 achieved was 0.74 moles per atom of wood carbon at an H/C ratio of 18.1. The gap between the actual and equilibrium production curves of CH_4 decreased with the increase in H/C ratio. This difference represents the effect of wood feeding rate on the CH_4 production. As the F/C ratio was increased by increasing the wood feeding rate, the difference between equilibrium and actual production of CH_4 increased. Therefore, it can be speculated that the increase in F/C ratio as well as the decrease in

hydrogen to wood carbon ratio were responsible for the decrease in the CH_4 production.

The equilibrium as well as actual production of CO, shown in Figure 5.10, decreased with the increase in the hydrogen to wood carbon ratio, but the gap between the actual and equilibrium production curves of CO increased with the decrease in H/C ratio. These changes can also be explained on a similar basis as those of CH_4. It seems that the production of CO also depended on the F/C ratio as well as the H/C ratio.

The equilibrium production of CO_2, as shown in Figure 5.11, increased with the decrease in H/C ratio, but a sharp increase was observed below an H/C ratio of 13. It was also found, as discussed previously, that the production of CO_2 also increased with the increase in F/C ratio. The actual and equilibrium production of CO_2 were the same at an H/C ratio of 8 but any change in this ratio increased the difference. Above an H/C ratio of 8, the actual production of CO_2 was more than the equilibrium production but below this value, the actual production was less than the equilibrium production. The presence of nickel catalyst may have been responsible for keeping the production of CO_2 low at low H/C ratios. As the partial pressure of CO_2

increased on the catalyst surface, the reduction of CO_2 to CO may have been the reason for low CO_2 production. The production of CO_2 was generally low during these experiments, probably due to the large excess of hydrogen present and the fact that the nickel catalyst also promoted the rate of the water gas shift reaction.

The production of water was calculated on the basis of change in hydrogen flow rate per hour per atom of wood oxygen fed per hour, i.e. H/O ratio. Above the H/O ratio of 20, a complete conversion of wood oxygen to H_2O is predicted under equilibrium conditions and there is no production of CO or CO_2. The actual production of water was always lower than the equilibrium production. The difference between these two curves, shown in Figure 5.12, depends mainly upon the production of CO and CO_2. This difference increased with the increase of H/O ratio up to the value of H/O ratio of 20 and then started decreasing. Hence, the production of H_2O may be only marginally dependent upon the F/C ratio but may be very much affected by the change in H/O ratio.

The actual production of all the gaseous products including water was also dependent upon the production of char and tar during an experiment. As the F/C ratio was increased, the relative production of char and tar

increased and the relative production of gases and water decreased. Because the amount of catalyst used and hydrogen flow rate were about the same during these experiments, the increase in F/C ratio decreased the H/C ratio as well as H/O ratio. On the basis of moisture free wood fed, the total production of char and tar increased from 7% at lowest F/C ratio (0.84 l/hr) to 32% at highest F/C ratio (3.68 l/hr). At low H/C or H/O ratios, i.e. when the wood feeding rates were very high, the limitation of amount of catalyst surface is believed to be the major cause of decrease in the production of gases and water. If during the experiments, the H/C or H/O ratio had been changed without changing the F/C ratio, the actual production of CH_4, CO, CO_2 and H_2O would be expected to be closer to their equilibrium production than was observed in the tests done.

Considering the total elemental balance of wood carbon and wood oxygen, it was observed that more than 83% of wood oxygen was converted to CO, CO_2 and H_2O, and 44% to 81% of wood carbon could be converted to CH_4, CO and CO_2 under experimental conditions. In addition to char and tar, there were always some other non-equilibrium gasification products such as C_2H_4, C_2H_6, etc. During the ultragasification of wood at high temperatures, the

production of C_2H_2 also was reported by Mok et al. (1984), but during the present experimental work, the gasification products were not analysed for the presence of C_2H_2. If C_2H_2 was produced during this process, it may have also consumed some of the wood carbon. However, at these lower temperatures, amounts of C_2H_2 likely to be formed would be negligible.

6. SUMMARY AND DISCUSSION OF MECHANISMS

6.1 Discussion of Product Yields

There are four main properties of a hydrogenation/cracking catalyst which affect the composition of products. These are:

(i) Cracking activity

(ii) Gasification activity

(iii) Hydrogenation activity

(iv) Coking activity

The alumina support contributes a strong cracking activity to the nickel catalyst. The cracking activity of alumina for the products of wood pyrolysis appears to be enhanced by the presence of nickel. The increase in the cracking activity of nickel catalyst on alumina support compared to that of alumina alone was discussed in Section 4.8. The degree of cracking accomplished by the catalyst is also, of course, dependent upon the temperature and the wood feeding rate.

Initially, the wood is pyrolysed thermally producing char, tar and a small quantity of gaseous products, including water. The fact that the amount of char produced in the catalytic gasification of wood is always very nearly the same as that produced by the

thermal pyrolysis of the wood at the same reaction conditions is the principal evidence for this conclusion. This is demonstrated in Figure 4.12, which is a reproduction of Figure 4.1, but showing the comparison of the char yields from the thermal and catalytic processes. This stage is followed by decomposition and gasification of the tar which probably is both thermally decomposed as well as catalytically cracked at the catalyst surface, although catalytic action would appear to be predominant. Catalytic cracking mainly produces CH_4 and other reformable products while thermal cracking on the surface would produce additional secondary char and CO_2 (Baker and Mudge, 1984). At low feed rates (or F/C ratio), little tar should be decomposed thermally because there are catalyst sites available for catalytic cracking and hydrogenation to take place. When the F/C ratio is increased, more catalyst surface could be occupied by tar molecules which would limit the sites available for adsorption of other reacting species, especially hydrogen or carbon monoxide. Therefore, as feed rate is increased with a fixed amount of catalyst, a point is apparently reached at which the catalyst surface is saturated with reactive species, and beyond this feed/catalyst ratio, less of the tar produced is cracked and hydrogenated, and

more thermal decomposition occurs. The result is the observed increase in tar and char produced, and in the amount of CO not methanated.

Hydrogenation activity of the catalyst is undoubtedly influenced by temperature and by hydrogen partial pressure on the catalyst surface. Acidity of the support also strongly affects the coking activity of a catalyst during tar cracking (Marshall, 1984). In this study, neither the hydrogen pressure nor the level of acidity of the catalyst support were studied systematically. Certainly, increased hydrogen pressure should have a very beneficial effect on the methanation reaction, and this variable would warrant further study.

The production of gaseous products per kg of wood fed decreases with increases in F/C ratio as shown by the calculated results given in Table 6.1. As the feed rate is increased a larger fraction of tar is apparently decomposed thermally which gives a smaller yield of gaseous products and significantly more tar and char (but the tar yield is still far less than that for uncatalyzed thermal pyrolysis, while the char yield is considerably more). The total gas production and composition are given in Table 6.1.

Table 6.1 : Gas Composition (H_2 free basis) with F/C Ratio, 550°C, Lab(3) Ni catalyst.

F/C Ratio, 1/hr	0.84	1.56	2.27	3.68
Total gas moles produced per kg of wood, mf	32.95	29.81	25.32	16.69
Gas production/hr/kg of catalyst	27.7	46.5	57.5	61.4
Gas Composition, % Volume				
CO	6.64	9.13	15.70	34.24
CO_2	2.22	5.14	10.41	17.62
CH_4	91.13	85.47	73.11	44.65
C_2 +	0.28	0.25	0.78	3.49

It is evident from these results that the fractional cracking of tar, methanation of CO and hydrogenation of small organic molecules on the catalyst decreases with increase in F/C ratio. In fact, a four fold increase in F/C ratio (0.84 to 3.68 l/hr) decreased the conversion to gas as well as the fractional conversion to methane by almost 50%. The yield of CO, CO_2 and of light hydrocarbons, other than CH_4, per unit of feed is increased with F/C ratio. As pointed out previously, however, the conversion to reformable carbon is much less affected, although it does decrease as the F/C ratio increases.

Cracking and gasification rates of the catalyst increase with temperature and the equilibrium relationships also change significantly above 550°C. The change in gas production and its composition is given in Table 6.2 showing the effect of temperature in the range of 400° to 650°C. The F/C ratio is not quite the same for all these experiments but varies in the range of 1.18 to 1.83 l/hr. A slight difference in the production of all gas components is expected due to this variation but such a small variation in F/C ratio is not likely to change any conclusions. The total gas production per kg of wood increases with temperature up to about 550°C and then becomes nearly constant. Due

Table 6.2 : Gas Composition (H_2 free basis) with Temperature, Lab(2) Ni catalyst.

Run No.	G-20	G-15	G-14	G-13	G-18	G-21
F/C Ratio, 1/hr	1.83	1.19	1.45	1.41	1.18	1.66
Temperature, °C	400	450	500	560	600	650
Total gas moles Produced per Kg of Wood, mf	19.09	23.12	28.53	31.02	33.57	32.94
Gas Composition, % volume						
CO	7.28	2.90	2.66	6.20	11.62	34.61
CO_2	5.98	1.68	1.51	3.67	5.07	6.98
CH_4	85.48	95.18	95.71	90.13	83.10	58.33
C_2 +	1.26	0.25	0.13	0.0	0.22	0.09

to higher F/C ratio at 650°C, the total gas production is slightly lower at 650°C than at 600°C. Equilibrium calculations based on CH_4 show (Section 5) that the methanation reactions are favored up to 500°C and the reaction equilibrium shifts towards the reverse reaction with further increase in temperature. Therefore, the selectivity for CH_4 increases with temperature up to 500°C and then this trend is reversed at higher temperatures.

$$CO + 3\ H_2 \text{ ===== } CH_4 + H_2O \qquad (6.1)$$

Production of CO increases at a faster rate as temperature increases than that of CO_2. Because water is also produced during methanation reactions, it is very likely that CO is the major source for any increased CO_2 production, via the water-gas shift reaction, which approaches equilibrium more closely at higher temperatures, although the equilibrium yield of CO_2 decreases somewhat over this temperature range.

$$CO + H_2O \text{ ===== } CO_2 + H_2 \qquad (6.2)$$

However, a certain amount of CO_2 is also produced as a primary product of the initial thermal pyrolysis of wood.

The variation of the production of water per unit mass of wood fed with F/C ratio and with temperature are presented in Table 6.3. As temperature increases, the amount of water produced per unit mass of wood increases up to 500°C and then starts to decrease. This behaviour is very similar to that of CH_4 production. Water is produced and consumed in various ways in this system. Some water is produced as a primary product of the initial thermal decomposition of wood. At low temperatures, the water yield is the sum of this primary water and the water produced from the methanation reaction of CO and small organic fragments on the nickel catalyst surface. As the yield of methane increases, so does the water yield until the temperature exceeds 500°C. Above this temperature, the equilibrium begins to favor the consumption of H_2O by reaction with CH_4 (the reverse of reaction 6.1) or by the shift reaction 6.2. As a result, the yield of H_2O decreases markedly as the temperature increases to 650°C.

Table 6.3 also shows that the water yield at constant temperature per unit of wood fed decreases largely because of the decreased catalytic fractional conversion of the wood to methanated gas. As discussed earlier (Section 4.7), this decrease appears to be due to the saturation of the available catalytic surface

Table 6.3 : Water Production with Temperature and F/C Ratio.

With Temperature (Lab(2) Ni Catalyst, 17% Ni)

Run No.	G-20	G-15	G-14	G-13	G-18	G-21
F/C Ratio, 1/hr	1.83	1.19	1.45	1.41	1.18	1.66
Temperature, °C	400	450	500	560	600	650
Water Production (% Wt. of wood, mf)	27.68	36.00	46.45	41.63	33.92	19.37

With F/C Ratio (Lab(3) Ni Catalyst, 8.8% Ni) 550°C

Run No.	G-51	G-49	G-52	G-50
F/C Ratio, 1/hr	0.84	1.56	2.27	3.68
Water Production (% Wt. of wood, mf)	48.91	40.33	31.95	20.26
Water Production/hr/gm of catalyst	0.411	0.629	0.725	0.746

with organic species or CO, with a consequent asymptotic approach to a maximum output of cracked and hydrogenated products, and therefore of water also.

As the cracking and gasification activities of the catalyst increases with increasing temperature at a constant wood feed rate (under an F/C ratio of 2), the tar production decreases. After the initial thermal pyrolysis of the wood, the tar is subsequently cracked and hydrogenated on the catalyst surface producing the major fraction of the gaseous products. At higher temperatures, the faster rates of cracking and hydrogenation of tar allows a greater production of gas, although the gas product composition changes due to equilibrium considerations. On the other hand, a slower cracking of tar at lower temperatures increases the yield of tar. As shown in Figure 4.3, the yield of tar at the lower F/C ratios is decreased from almost 20% at 400°C to only about 1% at 650°C.

An increase in feed rate (or F/C ratio) at constant temperature also increases the tar production. As the feed rate is increased, the available amount of catalyst appears to be inadequate. Presumably, more and more of the active surface of the catalyst is taken up by adsorbed CO or adsorbed small organic molecules produced by tar cracking. The number of active

catalyst sites occupied by hydrogen may be fairly constant, because of the high hydrogen content of the ambient gas, or may even be somewhat reduced as tar concentration increases. Therefore, the contact on the catalyst between reactive species formed due to cracking of tar, and hydrogen is reduced which subsequently reduces the degree of conversion of the tar, and more tar may remain uncracked. It can be seen in Table 4.11 that the tar yield increased from only 0.71% at F/C ratio of 0.84 l/hr to 18.4% at 3.68 l/hr.

In a recent publication (Klose and Baerns, 1984), it was stated that the rate determining step in methanation on nickel-alumina catalysts was the rate of the surface reaction to form $\cdot CH_2$ species. In our work, this rate would probably be limited at high F/C ratios by the supply of active adsorbed hydrogen. It is likely, therefore, that operation at higher H_2 pressure would allow higher methanation rates of wood.

There are two main sources for char production (Shafizadeh, 1982). Some char is formed directly from the pyrolysis of wood which is called primary char. Additional char, known as secondary char, is formed by thermal decomposition of tar. In a study of the catalytic steam gasification of wood, Baker and Mudge

(1984) suggested that tar decomposes due to thermal as well as catalytic reaction at the catalyst surface, but that it is only the thermal decomposition of the tar which produces secondary char.

The amount of char produced directly from the initial thermal pyrolysis of wood remains more or less the same as temperature increases, but the amount of secondary char produced by the decomposition of tar is very much affected by temperature. Catalytic decomposition of tar appears to be predominant at higher temperatures, rather than thermal decomposition, and therefore lesser amounts of secondary char are produced. As a result, total char production is reduced with increase in temperature. The total char production, presented in Table 4.8 decreased from 20.34% at 400°C to only 6.97% at 650°C. It is important to note here that for quantitative analysis of products, the carbon deposited on the catalyst was also included in the reported char yield. Therefore, the reported weight percent yield of char is actually a total of both primary and secondary chars.

As discussed previously, an increase in feed rate of wood appears to decrease the active catalyst sites available for catalytic decomposition of tar, and therefore, more tar is decomposed by thermal reactions

producing more secondary char. As a result, total char production was increased with increase in wood feed rate (or F/C ratio). Table 4.11 shows that the total char production was increased from 6.31% at the F/C ratio of 0.84 l/hr to 13.9% at F/C ratio of 3.68 l/hr.

6.2 Mechanism of Carbon Deposition on the Catalyst

Deactivation of nickel catalyst due to carbon decomposition or "coking" has been extensively studied by Moeller and Bartholomew (1982), Willey and Kittrell (1984), Ho and Harriott (1980) and Trimm (1977). A CO/H_2 gas mixture was adsorbed on the catalyst surface during all of these studies. Baker and Mudge (1984), however, studied deactivation by catalytic gasification of biomass in a steam atmosphere.

No specific attempts were made to study the mechanism of carbon decomposition on the nickel catalyst in the present study but based on the literature results cited above, a possible mechanism can be suggested. Reactions possibly causing carbon decomposition on a nickel catalyst include:

$$2\ CO \text{ ======= } C + CO_2 \qquad (6.3)$$

$$CH_4 \text{ ======= } C + 2\ H_2 \qquad (6.4)$$

$$C_nH_m(\text{light hydrocarbons}) \text{--- Polymer --- Coke} \qquad (6.5)$$

$$\text{Tars ---- Coke + Gases} \qquad (6.6)$$

Carbon can also be removed from the catalyst by gasification reactions that include the reverse of reactions 6.3 and 6.4, as well as the carbon-steam reaction:

$$C+H_2O \text{ --- } CO + H_2 \qquad (6.7)$$

The kinetics of coke formation are very much dependent upon the temperature, and several types of carbon (Trimm, 1977) are produced. Several investigations of methanation over nickel catalysts have provided evidence that adsorbed carbon is an active reaction intermediate and a precursor to the inactive forms of carbon.

Several types of carbon have been found by other researchers on nickel catalysts used for steam-reforming and methanation, depending upon the test conditions. Whisker carbon can be caused by the decomposition of CO, CH_4 and heavier hydrocarbons, whereas polymer and pyrolytic carbons generally occur only with heavier hydrocarbon feeds (Rostrup-Neilson, 1975).

In steam-reforming of hydrocarbons at low temperatures (below 500°C), coking usually takes the form of progressive deactivation by polymer formation on the nickel surface. Depending upon the reaction

conditions, feedstock and catalyst, this type of coking will not occur above a certain temperature.

At higher temperatures (above 450°C), whisker carbon formation predominates. Growth of this type of carbon does not cause a loss of intrinsic catalyst activity, but can cause deactivation when whiskers block the pores. Pyrolytic carbon deposition can occur on the catalyst surface at higher temperatures also, and can cause deactivation by pore blockage.

Baker and Mudge (1984) showed by using model compounds that ethylene and phenol (representing reactions 6.5 and 6.6) are more likely to cause carbon deposition at gasification conditions than are methane and carbon monoxide. They concluded that the cracking of light hydrocarbons and tars on the catalyst is the primary cause of carbon decomposition in the laboratory gasifier. From tests done at 750°C, they also concluded that (i) Ni on α-alumina, has very low carbon deposition in comparison to other catalysts, (ii) more acidic supports had more carbon deposition, and (iii) cracking of tars on the support is the predominant cause of carbon deposition.

The present study also supports the conclusions made by Baker and Mudge (1984). The amount of carbon deposited

on nickel catalysts is related to the amount of tar cracked. With increase in temperature, the yield of tar decreases the amount of carbon deposited on the nickel catalyst appears to increase somewhat. The experimental values, obtained by direct measurement of the carbon content of used catalyst, are shown in Table 6.4. Comparison of tests at about the same F/C ratio shows clearly the increase in carbon deposition as temperature increases.

As proposed earlier, as the wood feeding rate increases, thermal decomposition of tar also increases and the extent of catalytic cracking of tar is reduced. More char production and carbon deposition on the catalyst will then occur due to the thermal decomposition of tar. Because the F/C ratio was highest at 400°C among all the experiments listed in Table 6.4, the carbon deposition was higher than expected at 400°C. On the other hand, due to the lowest F/C ratio at 600°C, carbon deposits on the catalyst were lower than expected. However, Runs G-15 and G-18 give a good comparison, as do Runs G-14, G-13 and G-21.

The increase in carbon deposition with increase in feed rate is more evident from Table 6.5, which shows that, as wood feeding rate (or F/C ratio) was increased,

Table 6.4 : Carbon Deposition on Nickel Catalyst with Temperature, Lab(2) Ni catalyst.

Run No.	G-20	G-15	G-14	G-13	G-18	G-21
F/C Ratio, 1/hr	1.83	1.19	1.45	1.41	1.18	1.66
Temperature, °C	400	450	500	560	600	650
Tar Yield (Wt. % of wood, mf)	19.68	14.30	4.78	1.33	3.35	1.37
Wt. % of carbon on the catalyst (% of catalyst weight)	4.54	2.93	3.24	3.55	3.06	4.95

Table 6.5 : Carbon Deposition on Nickel Catalyst with F/C Ratio, 550°C, Lab(3) Ni catalyst.

Run No.	G-51	G-49	G-52	G-50
F/C Ratio, 1/hr	0.84	1.56	2.27	3.68
Tar Yield (Wt. % of wood, mf)	0.71	0.48	2.66	18.40
Wt. % of Carbon on the Catalyst	3.44	6.11	11.07	14.20

carbon deposition on the catalyst also increased. According to Trimm (1977), the formation of coke on catalytic nickel is largely independent of effects from the support material. The very high accumulation of secondary carbon on the catalyst at the high F/C ratios may also partly explain the reduction in cracking and hydrogenation activity observed, presumably due primarily to de-activation of the metallic nickel.

7. CONCLUSIONS

Experimental studies have shown that wood can be gasified catalytically at low temperatures (500°-550°C) with a carbon conversion to gases of over 80%. Methane can be produced with a selectivity based on carbon gasified, of 95% or more, giving a yield of 70-75% methane based on carbon fed to the reactor. Including the water of reaction, a gas yield of 94% or more can be obtained. The above results are for reaction in a hydrogen atmosphere carried out at one atmosphere total pressure over a nickel-alumina catalyst in a single fluidized bed reactor.

Somewhat higher yields of reformable gases (CH_4 + CO + other hydrocarbons) can be obtained at higher temperatures e.g. 650°C but with a considerable loss in methane selectivity. The high methane selectivity is due largely to the low temperature of gasification.

The effects of feed to catalyst ratio have also been investigated, and it appears that a feed/catalyst weight ratio of about 2 h^{-1} or less should be used. This value is essentially the same as that used for ordinary thermal pyrolysis for the production of liquids from biomass utilizing the Waterloo Fast Pyrolysis process. In addition, temperatures and vapor residence times are the same for

gasification as for the Waterloo Fast Pyrolysis process, so that the same reactor technology can be used for both systems.

Nickel-on-alumina catalysts performed more satisfactorily than did ruthenium or cobalt-molybdenum catalysts. The nickel loading on an alumina support (surface area 30-60 m^2/g) should be at least 9% nickel content. The nickel catalyst can be readily regenerated by oxidation of carbon deposits with little apparent loss in activity. Catalyst life time is uncertain as limitations in achieving extended periods (over 2 hours) of continuous uniform sawdust feed led to inconclusive results.

Although nickel-on-alumina catalysts prepared in our laboratories were used for these studies in order to ensure control of catalytic parameters, industrial nickel-alumina catalysts performed more or less as effectively in preliminary tests, and suitable commercial catalysts are available, therefore.

Carbon deposition on the catalyst is low at lower temperatures and feed/catalyst ratios of less than two. The carbon deposit (about 3%-4% of the catalyst weight) did not seem to affect the activity particularly, nor did continuous accumulation appear to occur. There was some evidence, from

a single experiment, that carbon dioxide in the feed might aid in limiting carbon deposition.

Equilibrium calculations showed that at temperatures of 500°C or less, the principal gasification products should be CH_4 and H_2O, but some CO and CO_2 as well as small amounts of C_2 + hydrocarbon gases were also always formed. At high temperatures of about 650°C, the products approached closely their equilibrium values.

The results of a study of the various system parameters resulted in a preliminary model of the catalytic gasification process. The wood initially undergoes fast thermal pyrolysis, just as occurs in the Waterloo Fast Pyrolysis process, with the same high yield of liquids and gases. The liquid vapors are then adsorbed on the catalyst surface where cracking followed by hydrogenation takes place. The cracking occurs on the support as well as on the nickel, and the support cracking activity is greatly enhanced by the presence of nickel, perhaps by allowing the total decomposition process to proceed. The tar vapors probably decompose on the catalyst surface to CO, H_2O and small organic molecules. The CO and small organic molecules are readily hydrogenated by the nickel to methane. It is suggested from our own results, as well as those of others, that the hydrogenation step to form the necessary CH_2

species on the surface is probably the rate controlling step. From this result, it is concluded that operation at higher hydrogen pressures would be beneficial.

The nature of a complete gasification process using the concepts developed in this work is illustrated in Figure 7.1. Wood is methanated in the gasifier, and after removal of the char the methane-rich gas (95% or more CH_4 by volume on a hydrogen and moisture free basis) is heated with added water, if necessary, and sent to a conventional catalytic steam reformer. Here the CH_4 is converted to a $CO + 3\ H_2$ mixture (approximately). After heat exchange, part of this stream is compressed and sent to a membrane permeation unit which will produce two streams, one rich in H_2 with much of the CO_2 content also, and the other rich in CO. Membrane separators for gases, for example of the Monsanto "Prism" type, or equivalent, are available as fully developed commercial technology. The H_2-CO separation is one of the easiest to accomplish in this type of diffuser. The CO-rich stream is blended with the product from the steam-reformer to give the required $CO + H_2$ mixture to maintain the system balance. The H_2-rich stream goes to the gasifier. An idealized sequence of reactions occurring could be written as:

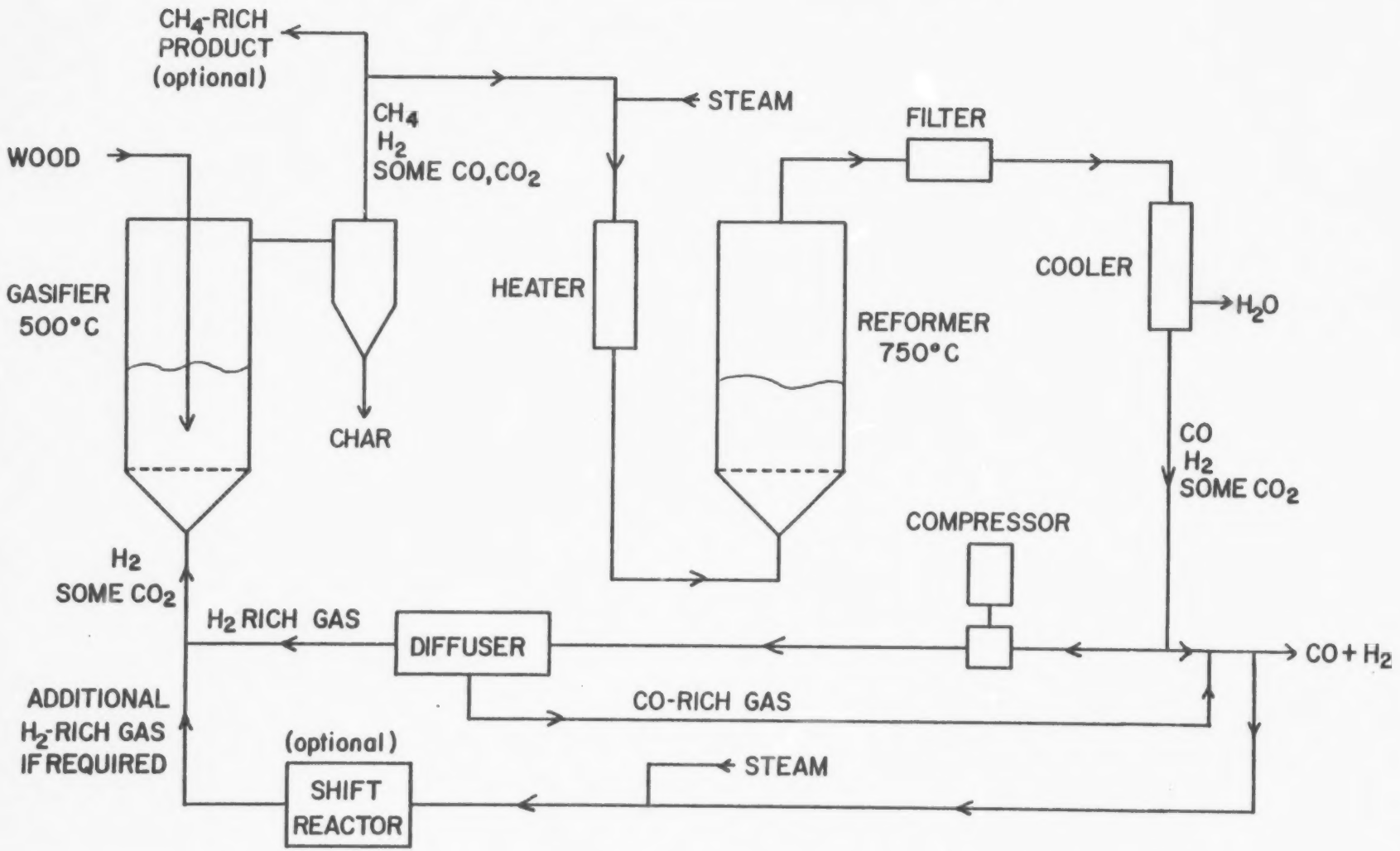


Figure 7.1 Schematic of Integrated Gasification Process for Production of Methane-Rich Gas and/or Synthesis Gas from Wood

(1) $2\ C_6H_9O_4 + 23\ H_2 \longrightarrow 12\ CH_4 + 8\ H_2O$ (some CO, CO_2)
(wood)

(2) $12\ CH_4 + 12\ H_2O \longrightarrow 12\ CO + 36\ H_2$

(3) $12\ CO + 36\ H_2 \longrightarrow 4.33\ CO + 13\ H_2$ (to product gas)

$7.67\ CO + 23\ H_2$ (to diffuser)

(4) $7.67\ CO + 23\ H_2 \longrightarrow 23\ H_2$ (to gasifier)

$7.67\ CO$ (to product gas)

The final overall result of the gasification system is given by

(5) $2\ C_6H_9O_4 + 4\ H_2O \longrightarrow 12\ CO + 13\ H_2$

The proposed gasification system has the unique characteristic of being oxygen and hydrogen deficient so that water must be added to produce synthesis gas. No dilution of the synthesis gas by N_2 occurs, and very little sulfur or nitrogen oxides are formed. The process differs from steam gasification in which a high temperature is required to give adequate reaction rates of steam with wood, even if a catalyst is used. This high temperature prevents high yields of methane being achieved, as can be done in our method at the lower temperature of operation.

In comparison to methane produced from bio-gas fermentation methods, our method gives nearly twice the yield of CH_4 per kg of organic material, and the gas produced could contain up to 80% to 85% CH_4. Also process equipment sizes are much smaller for the catalytic gasification method.

The proposed system also has great flexibility, in that a high heating value methane-rich gas and a syngas could be produced simultaneously by shifting a part of the syngas product to produce additional hydrogen, which would allow the additional wood to be gasified for a CH_4-rich stream. This option is also shown in Figure 7.1.

In practice, syngas would also be produced from the small amounts of tar and higher hydrocarbons which would be decomposed in the steam reformer. In fact, only the char would not appear in the final gas product.

The gasification reaction itself is highly exothermic and heat must be removed from the gasifier. The steam reforming is endothermic and the overall process is somewhat endothermic. Char could be used as the necessary source of process heat.

Operation of the proposed gasification system under pressure would be advantageous. As concluded in this work, the gasification reaction would be promoted by higher H_2 pressures. The cost of compressing gas for the diffusional unit would be minimized and the product gas would be delivered at higher pressure. Operation to 2 or 3 M Pa should present no new problems, and known technology should be useable.

A preliminary feasibility study of the Waterloo Fast Pyrolysis process has recently been completed by BBC Engineering Ltd. (Black, 1986). Using the costs given in this study as a basis, and substituting a steam reforming and diffusional separation step for the liquid product collection step, an order-of-magnitude estimate of gas product cost was made for a 100 tonne/day dry wood feed plant. It was assumed that green wood waste (40% moisture) at $40 BDT was used as feed. Capital was taken to be 50% / 50% debt / equity ratio, and a 30% return on equity was assumed. On this basis, a CO + H_2 mixture can be produced for 8c to 9¢/m^3. This cost would be most sensitive to the cost of the wood feed and to the wood drying and grinding costs, which would represent about 60% of both capital and operating costs. At this level of production, the cost of the syngas would be nearly competitive with syngas made from natural gas costing 17¢/m^3. However, these are very preliminary figures, and may be ±30% in error. A larger scale plant would be less costly per unit of product, but it is felt that one of the advantages of the present concept is that it appears to be easily operable on a small scale.

Another feature of the process which could be overlooked is that no waste products (except possibly flue gas from char burning) are produced. All water produced or added is consumed in the process. No tar would be produced, because

it would be reformed in the steam reformer. Depending on operating considerations, some CO_2 might be removed from the product gas as a by-product, if desired. As a consequence, the proposed process should have no environmental concerns.

While a detailed cost estimate was not carried out, it is apparent that, depending on the cost of the biomass feed, the proposed gasification process could probably produce a methane-rich gas competitively or even at a considerably lower cost than the cost of biogas. If wood were used as the feed material for both processes, then the gasification process proposed here would undoubtedly be a cheaper source of methane than a bio-gas route and would involve considerably less capital cost also.

8. RECOMMENDATIONS

As a result of the encouraging results from the present investigation, the following recommendations can be made.

a) The effect of pressure operation on CH_4 production rate per unit of catalyst, and on the selectivity of the gasification reaction should be investigated.

b) The performance of one or more appropriate industrial nickel-on-alumina catalysts should be fully evaluated, particularly for an extended period of operation.

c) The benefits of addition of CO_2 to the inlet hydrogen stream to the gasifier as a way of minimizing carbon deposition should be investigated. Some characterization of surface carbon deposits would be helpful.

d) The performance of a membrane diffusion unit to separate the $H_2 + CO_2$ components from the CO should be evaluated e.g. Monsanto "Prism" type. This system (H_2 from CO) represents one of the easiest to separate.

e) An integrated, preferably pressurized complete gasification system with a throughput of about 100 g/h should be built and tested to study the overall performance of the interconnected gasifier, reformer and diffuser, and to construct a mathematical model of the process.

f) A test should be carried out at atmospheric pressure in the large 3 kg/h Waterloo Fast Pyrolysis reactor, operated as an atmospheric pressure catalytic gasifier.

g) A more complete cost analysis should be carried out when data on integrated system performance is available.

h) Nickel-Ruthenium catalysts have been reported as having significantly longer active lifetime, more resistance to carbon deposition under high pressure and high conversion conditions than nickel catalyst. Bimetallic methanation catalysts such as Ni-Ru and Ni-Pt should also be tested for wood gasification.

i) TiO_2 as catalyst support reportedly enhances the specific activity for CO hydrogenation over metals such as Ni, Pt. This may prove very favorable for CO hydrogenation under lower hydrogen partial pressures. Possible improvement in the catalyst performance should be investigated using TiO_2 as the catalyst support in place of Al_2O_3. It may also be worthwhile to investigate other supports which have been used for cracking such as MgO and ZrO_2.

j) Inasmuch as a constant H_2 supply was used in this work with a variable amount of wood feed, the amount of excess hydrogen over the stoichiometric requirement varied in most runs. At lower F/C ratios of around 1, the excess H_2 was around 300% to 400%, while at the higher F/C ratios (3.5 or more) the H_2 was close to the stoichiometric requirement. Further tests should be done with a constant excess of H_2 in the reactor.

REFERENCES

Antal, M.J.,Jr., (1985); "Biomass Pyrolysis: A Review of the Literature - Part 2 - Lignocellulose Pyrolysis" Advances in Solar Energy, K.W. Boer and J.A. Duffie (Eds.) Vol. 4, pp. 175-255

Baker, E.G. and L.K. Mudge, (1984); "Mechanism of Catalytic Biomass Gasification", J. Anal. Appl. Pyro., 6, pp. 285-297

Ho, S.V. and P. Harriott, (1980); "The Kinetics of Methanation on Nickel Catalysts", J. Catalysis, 64, pp. 272-283

Klose, J. and M. Baerns, (1984); "Kinetics of the Methanation of Carbon Monoxide on an Alumina-Supported Nickel Catalyst", J. Catalysis, 85, pp. 105-116

Marshall, A., (1984); "Catalytic Conversion of Pyrolysis Oil in the Vapor Phase" M.A.Sc. Thesis, Dept. of Chemical Engineering, University of Waterloo, Waterloo, Canada

Moeller, A.D. and Bartholomew (1982); "Deactivation by Carbon of Nickel, Nickel-Ruthenium and Nickel-Molybdenum Methanation Catalysts", Ind. Eng. Chem. Prod. Res. Dev., 21, pp. 391-397

Mok, L.K., R.G. Graham, R.P. Overend, B.A. Freel and M.A. Bergougnou, (1984); "Ultrapyrolysis: The Continuous Fast Pyrolysis of Biomass" Bio. Energy 84, H. Egnius and A. Ellegard (Eds.), Vol. III, pp. 23-30, Elsevier App. Sc. Publ. (London)

Perry, R.H. and D. Green (Eds.), 1984); "Chemical Engineers Handbook", 6th Edition, McGraw-Hill, New York, pp. 8-84

Scott, D.S. and J. Piskorz, (1982a); "The Flash Pyrolysis of Aspen Poplar Wood", Can. J. Chem. Eng. 60, pp. 666-674

Scott, D.S. and J. Piskorz, (1982b); "A Low Rate Entrainment Feeder for Fine Solids" Ind. Eng. Chem. Process Des. Devel. 21 pp. 319-322

Scott, D.S. and J. Piskorz, (1984); "Production of Liquids from Biomass by Continuous Flash Pyrolysis", Bioenergy 84, Vol. III, pp. 15-22, H. Egneus and A. Ellegard (Eds.), Elsevier App. Sci. Publ., London

Scott, D.S., J. Piskorz and D. Radlein, (1985); "Liquid Products from the Continuous Flash Pyrolysis of Biomass", Ind. Eng. Chem. Process Des. Dev., 24, pp. 581-588

Shafizadeh, F., (1982); "Introduction to Pyrolysis of Biomass", J. Anal. App. Pyrol., 3, pp. 283-305

Stiles, A.B., (1983); "Catalyst Manufacture - Laboratory and Commercial Preparations", Marcel Dekker Inc., New York, pp. 119-120

Suzuki, et al., (1984); "Hydrogasification of Wood for High Heating-Value Gas Production", Makuzai Gakkaishi, 30 (8), pp. 684-692

Trimm, D.L., (1977); "The Formation and Removal of Coke from Nickel Catalyst", Catal. Rev.-Sci. Eng., 16 (2), pp. 155-189

Vogel, A.I. (1961); "A Text Book of Quantitative Inorganic Analysis", 3rd Edition, Longman Group Ltd., London, pp. 479-481

Willey, R.J. and J.R. Kittrell, (1984); "Fluidized-Bed Deactivation Model for a Methanation System", Ind. Eng. Chem. Prod. Res. Dev., 23, pp. 206-208

TABLES

Table 3.1	Summary of the Gas Chromatographic Procedure Used for the Analysis of Gaseous Products
Table 4.1	Pyrolysis of Wood IEA Standard Poplar Wood, Ottawa Sand
Table 4.2	Typical Chemical and Physical Properties Catalysts G-33RS, G-65RS, G-65 and Lab (1)
Table 4.3	Results of Experiments with G-65 and G-65RS Ni Catalysts
Table 4.4	Results of Experiments with G-33RS Ni Catalyst
Table 4.5	Results of Experiments with Lab (1) Ni Catalyst
Table 4.6	Effect of Nickel Content of Catalyst Residence Time 0.44 s
Table 4.7	Effect of Hydrogen Partial Pressure on Gasification Products on Nickel Catalyst Lab (5) Ni Cat. (30% Ni), 550°C
Table 4.8	Effect of Temperature on Gasification Products Lab (2) Ni Catalyst (17% Ni), Res. Time 0.43-0.45 s
Table 4.9	Effect of Residence Time on Gasification Products Lab (2) Ni Catalyst (17% Ni)
Table 4.10	Effect of F/C Ratio, 550°C, 0.44 s
Table 4.11	Effect of F/C Ratio on Lab (3) Ni Catalyst, 550°C, Residence Time 0.44 s
Table 4.12	Effect of Hydrogen Atmosphere on the Alumina Support (Al-1404, Harshaw), 550°C, 0.44 s
Table 4.13	Hydrogasification with Different Materials at 550°C
Table 4.14	Effect of Catalyst Regeneration 560°C, 0.44 s, Lab (2) Ni Catalyst (17% Ni)
Table 4.15	Hydrogasification of Wood vs. Cellulose Lab (2) Ni Catalyst, 17% Ni, 500°C, 0.44 s
Table 4.16	Hydrogasification of Char

Table 4.17 Hydrogasification of Ruthenium Catalyst and Comparison with Nickel Catalysts

Table 4.18 Comparison of Gasification Yields with a Cobalt-Molybdenum Catalyst and a Nickel Catalyst

Table 4.19 Gasification with 50% CO and 50% H_2 Gas Mixture Lab (3) Ni Catalyst, 8.8% Ni, 550°C, 0.44 s

Table 4.20 Gasification of Wood in Presence of 33% CO_2 and 67% H_2 Gas Mixture, Lab (3) Ni Catalyst (8.8% Ni)

Table 4.21 Wood Gasification with Industrial Catalysts

Table 4.22 Study of Catalyst Lifetime, Lab (3) Ni Catalyst, 8.8% Ni, 550°C, 0.44 s

Table 5.1 Production per Atom of Gas Element (C or O) at Different F/C Ratio, Lab (3) Ni Catalyst, 550°C

Table 6.1 Gas Composition (H_2-free basis) with F/C Ratio, 550°C, Lab (3) Ni Catalyst

Table 6.2 Gas Composition (H_2-free basis) with Temperature, Lab (2) Ni Catalyst

Table 6.3 Water Production with Temperature and F/C Ratio

Table 6.4 Carbon Deposition on Nickel Catalyst with Temperature, Lab (2) Ni Catalyst

Table 6.5 Carbon Deposition on Nickel Catalyst with F/C Ratio, 550°C, Lab (3) Ni Catalyst

ILLUSTRATIONS

Figure 3.1 Process Flow Diagram for Catalytic Hydrogenation of Wood

Figure 3.2 Diagram of Solids Feeder

Figure 3.3 Effect of Different Gas Rates and Stirring Speeds on Sawdust Feed Rate. Poplar Wood, 149 - 250 μm

Figure 3.4 Diagram of the Catalytic Reactor and Cyclone Assembly

Figure 4.1 Effect of Nickel % in the Catalyst on Gasification Products, 550°C, H_2 Atmosphere, 0.44 s

Figure 4.2 Effect of Nickel % in the Catalyst on Gaseous Products, 550°C, H_2 Atmosphere, 0.44 s

Figure 4.3 Effect of Temperature on Gasification Products Lab (2) Ni Catalyst, H_2 Atmosphere, 0.44 s

Figure 4.4 Effect of Temperature on CO and CO_2 Production Lab (2) Ni Catalyst, H_2 Atmosphere, 0.44 s

Figure 4.5 Effect of Temperature on Gas and CH_4 Production Lab (2) Ni Catalyst, H_2 Atmosphere, 0.44 s

Figure 4.6 Effect of Temperature on Reformable Gas Carbon and Selectivity for CH_4, Lab (2) Ni Cat., H_2 Atmos.

Figure 4.7 Effect of F/C Ratio on Gasification Products Lab (3) Ni Catalyst, 550°C, H_2

Figure 4.8 Yield of CH_4, CO and CO_2 with F/C Ratio Lab (3) Ni Catalyst, 550°C, H_2

Figure 4.9 Change in Reformable Carbon in Gas with F/C Ratio Lab (3) Ni Catalyst, 550°C, H_2

Figure 4.10 MANUFACTURER'S SPECIFICATIONS FOR CATALYSTS
Ni-3266 E, 1/16", Nickel Catalyst
Ni-0901 S 1", Nickel Catalyst
G-65 Nickel Catalyst
C11-9-02 Nickel Catalyst

Figure 4.11 Yield of CH_4 and CO with Time IEA Poplar Wood, H_2, Lab (3) Ni Catalyst, 550°C

Figure 5.1 Effect of Temperature on Equilibrium and Actual Production of CH_4, Lab (2) Ni Catalyst, 0.44 s

Figure 5.2 Effect of Temperature on Equilibrium and Actual Production of H_2O, Lab (2) Ni Catalyst, 0.44 s

Figure 5.3 Effect of Temperature on Equilibrium and Actual Production of CO, Lab (2) Ni Catalyst, 0.44 s

Figure 5.4 Effect of Temperature on Equilibrium and Actual Production of CO_2, Lab (2) Ni Catalyst, 0.44 s

Figure 5.5 Effect of F/C Ratio on Equilibrium and Actual Production of CH_4, Lab (3) Ni Catalyst, 550°C

Figure 5.6 Effect of F/C Ratio on Equilibrium and Actual Production of H_2O, Lab (3) Ni Catalyst, 550°C

Figure 5.7 Effect of F/C Ratio on Equilibrium and Actual Production of CO, Lab (3) Ni Catalyst, 550°C

Figure 5.8 Effect of F/C Ratio on Equilibrium and Actual Production of CO_2, Lab (3) Ni Catalyst, 550°C

Figure 5.9 Effect of H_2 Partial Pressure on Equilibrium and Actual Production of CH_4, 550°C

Figure 5.10 Effect of H_2 Partial Pressure on Equilibrium and Actual Production of CO, 550°C

Figure 5.11 Effect of H_2 Partial Pressure on Equilibrium and Actual Production of CO_2, 550°C

Figure 5.12 Effect of H_2 Partial Pressure on Equilibrium and Actual Production of H_2O, 550°C

Figure 7.1 Schematic of Integrated Gasification Process for Production of Methane-Rich Gas and/or Synthesis Gas from Wood

Appendix (A)

A ruthenium catalyst containing 1.5% ruthenium on alumina (named Lab (6) Ru) was prepared in this laboratory according to the procedure described by Stiles [1] :

Reagents :

Ruthenium (III) chloride, hydrate; RuCl .3 H O, Engelhard Corporation

Alumina catalyst (Al-1404 T 3/16"), Harshaw Chem. Co.

Sodium bicarbonate, $NaHCO_3$, Baker Chem. Co.

(1) Alumina tablets were crushed and screened to get 332 g of paricles in the size range of 250 - 590 um.

(2) A sodium bicarbonate solution was prepared by dissolving 36 g of sodium bicarbonate in 217 g of distilled water.

(3) A ruthenium trichloride solution was prepared by dissolving 13.075 g of $RuCl_3 .3 H_2O$ in 292 g of distilled water.

(4) The alumina particles were coated with the sodium bicarbonate solution in Boston Ratiopax - I coating device.

(5) The alumina, moist with sodium bicarbonate, was removed from coating device and dried in an oven at 110°C.

(6) The dry alumina particles impregnated with sodium bicarbonate was returned to coating device and were then coated with ruthenium trichloride solution.

(7) The ruthenium trichloride solution was sprayed onto the alumina particles and because of the presence of sodium bicarbonate, the ruthenium was deposited as a thin coating on the periphery of the support material.

(8) The rotation of coating device was continued for 30 minutes to ensure complete precipitation of ruthenium and then distilled water was added to the coating device and was allowed to overflow untill such time as all the sodium that was extractable was removed from the particles.

(9) The washed catalyst was then removed from the coating device and dried at 150°C.

REFERENCE

(1) Stiles, A. B. ; "Catalyst Manufacture - Laboratory and Commercial Preparations", Marcel Dekker Inc., New York, 1983, pp 121-122.

APPENDIX (B)

The nickel content of the catalyst was determined by gravimetric analysis using an alcoholic solution of dimethylglyoxime. The procedure used is given described in following steps (2) :

(1) 250 mg of the Lab(2) nickel catalyst was dissolved by warming with 40 ml of 10N-hydrochloric acid.

(2) 10 ml of 11N-nitric acid was added and the solution was boiled gently to expel the oxides of nitrogen, if any.

(3) The resulting solution was diluted to 200 ml and was heated nearly to boiling.

(4) 25 ml solution of 25 % tartaric acid was introduced and it was nutralized with 28 % aqueous ammonia solution until a faint odor of ammonia was detected in the vapors over the solution.

(5) The solution was made slighty acidic with hydrochloric acid and was heated to 70°C.

(6) 20 ml of the 1 % alcoholic solution of dimethylglyoxime was added (1 ml of this solution was sufficient for the precipitation of 2.5 mg of nickel).

(7) Sufficient 28 % aqueous ammonia solution was introduced until a slight excess was present as indicated by the odor, plus an additional 2 ml.

(8) The solution was digested for 1 hour at about 60°C.

(9) The precipitates were allowed to stand and cool for 1 hour.

(10) The cold solution was filtered through a porcelain

filtering crucible, previously heated to 115°C for 2 hours and weighed after cooling in a desicator.

(11) The precipitates were throughly washed with water.

(12) Finally, the crucible and contents were dried at 120 °C for 2 hours and allowed to cool in a desicator and weighed.

(13) The precipitates, $Ni(C_4H_7O_2N_2)_2$ contained 20.31 % of nickel.

On calculation, it was found that Lab(2) nickel catalyst contained approximately 17 % nickel.

CALCULATION OF MATERIAL AND ELEMENT BALANCE

A complete material and carbon balance procedure for one typical run is given below. The log sheet and computer results sheet for that run are also attached.

Run No. G-13 Date Feb. 28, 1985

Run Description Lab(2) Ni Catalyst (17% nickel), H_2 Atmosphere
IEA Poplar Wood, 105-250 um, 4.32% moisture

Run Temperature 560 ^{0}C

Run Time 29 minutes

Total Wood Fed 33.72 g

Total moisture free Wood Fed = 33.72 (1 - 0.0432) = 32.263 g

Weight of catalyst used 47.4 g

(1) Calculation of Residence Time

Total H_2 Gas Feed Rate (25 ^{0}C, 1 atm.) = 4.0+0.2+1.5
= 5.7 l/min.

Catalyst Particle Density = 1.274 g /cc

Catalyst particle Volume = 47.4/1.274 = 37.21 cc

Reactor Space Volume = 15" - 37.21 = 117.79 cc

Residence Time -

$$\frac{117.79 * (273+25) * 60}{5.7 * (273+560) * 1000} = \underline{0.44} \text{ s}$$

(2) Calculation of F/C Ratio

$$\text{F/C Ratio} = \frac{\text{Total moisture free feed} * 60}{\text{Catalyst Weight} * \text{Run Time in min.}}$$

$$= \frac{32.263 * 60}{47.4 * 29} = \underline{1.41} \text{ l/hr}$$

(3) Calculation of Gaseous Products

Total Gas Collected in Bag = 5.34 ft^3 = 151.212 l

Gas Chromatograph Analysis; 25 ^0C; 1 atm, Residual Gases

Component	% Volume (by G.C.)	Volume (l)	Density (g /l)	Mass (gm)	% Weight of feed, mf
CO	0.9925	1.5008	1.1442	1.7172	5.3225
CO_2	0.5867	0.8872	1.8182	1.6130	4.9996
CH_4	14.4272	21.8157	0.6622	14.4463	44.7768
C_2H_4	0.0	0.0	1.1494	0.0	0.0
C_2H_6	0.0	0.0	1.2270	0.0	0.0
C_3	0.0	0.0	1.7678	0.0	0.0
C_4+	0.0	0.0	2.65	0.0	0.0
Total	16.0064	24.2037		17.7765	55.0989

(4) Calculation of Water

Water Content of Vial(s) Oil = 98.27%
Water in Vial(s) = (11.32 + 0.76)*98.27/100 = 11.871 g

Water Percent in wash oil = 1.848%
Water in Wash Oil = (241.36 - 113.28)*1.848/100 = 2.367 g

Water in Gaseous Form (in Gas Bag)

Calibration for Gas Chromatograph for Water
5.71 ug Water Gives a Peak of Area 0.25737

Peak Area for 1 cc of Product Gases = 0.2078

Water in Product Gases

$$\frac{0.2078 * 5.71 * 10^{-6} * 1000 * 151.212}{0.25735} = 0.697 \text{ g}$$

Total Water in Products = 14.935 g

Water in Washing Methanol = 0.036%
Water Added with Washing Methanol -
(241.36 - 113.38) * 0.036/100 = 0.046 g

Moisture in Wood = 33.72 * 4.32/100 = 1.457 g

Total Water Added = 1.503 g

Total Mass of Water Produced During Process = 13.432 g

Water Production as Weight % of Feed. mf = 41.633 %

(5) Calculation of Char

Weight Change in (Reactor + Cyclone) Assembly = 1.85 g

Char on Filter Paper = 0.46 g

Catalyst Weight Loss on N2 Purging = 0.07 gm
Catalyst Weight Loss on Reduction
(0.64 - 0.07) * 16/18 = 0.507 gm
Total Loss in Catalyst Weight = 0.577 g

Weight Loss in Reactor = 0.02 g

Total Char = 2.907 g

Char Production as Weight % of Feed, mf = 9.010 %

(6) Calculation of Tar

Tar Collected on Glass-Wool Filter(s) = 0.12 g

Tar Content of Vial Oil = 100 - 98.27 = 1.73%
Tar in Vial(s) = (11.32 + 0.76)*1.73/100 = 0.209 g

Tar Collected after Evaporation = 113.38-113.28 = 0.10 g

Total Tar Production = 0.429 g

Tar Production as Weight % of Feed = 1.330 %

(7) Total Yields, Weight % of moisture-free Feed

(a)	Gases	55.099 %
(b)	Water	41.633 %
(c)	Char	9.010 %
(d)	Tar	1.330 %
	Total Yields	107.072 %

(8) Example of Carbon Balance

Weight of moisture-free Wood Fed = 32.263 g
Carbon Content of moisture-free Wood = 48.495 %

Total Carbon Fed = 15.646 g

(a) Carbon in Char

By Elemental Analysis -
Carbon in Deactivated Catalyst (in Reactor) = 3.55 %
Carbon in Char (Cyclone + Char Pot + Filter Paper) = 66.39 %

Weight of Deactivated Catalyst

Weight of Catalyst Used	= 47.4	g
Weight Change in (Reactor + Cyclone)	= 1.85	g
Weight Loss in Reactor	= 0.02	g
Total	= 49.27	g

Char Collected in (Char Pot + Cyclone) = 1.17 gm

Weight of Deactivated Catalyst in the Reactor
49.27 - 1.17 = 48.10 g

Carbon on Deactivated Catalyst = 48.10 * 3.55/100 = 1.708 g

Carbon in Char (Char Pot + Cyclone + Filter Paper)
(1.17 + 0.46) * 66.39/100 = 1.082 g

Total Carbon (Reported as Carbon in Char) = 2.790 g

Carbon in Char as Weight % of C in Feed = 17.832 %

(b) Carbon in Tar

Approximate Carbon Content of Tar (for all Runs) = 55 %

Carbon in Tar = 0.429 * 0.55 = 0.236 g

Carbon in Tar as Weight % of C in Feed = 1.508 %

(c) Carbon in Gases

C in CO	= 1.7121 * 12/28	= 0.7359	g
C in CO_2	= 1.6130 * 12/44	= 0.4399	g
C in CH_4	= 14.4463 * 12/16	= 10.8347	g
C in $C_2H_4 + C_2H_6 + C_3 + C_4^+$		= 0.0	g

Total Carbon in Gas = 12.0105g

Carbon in Gas as Weight % of C in Feed = 76.764 %

Total Carbon Yield -

C in Gas	76.764 %
C in Tar	1.508 %
C in Char	17.832 %
Total Carbon Yield	96.104 %

LOG SHEET OF RUN G-13

RUN # G-13 DATE Feb 28, 85

CATALYST TYPE Ni Cat. #2

MAIN PARTICLE SIZE (−60 + 140) mesh MOISTURE : 4.32%

INITIAL REACTOR TEMPERATURE 530° C

1. BEFORE RUN

(a) BED (−30+60) mesh 47.4 g

(b) FLUIDIZATION GAS RATE 4.0 L/Min
FEEDER ~~tube~~ GAS FLOW 0.2 L/Min.
FEEDER ~~TOP~~ tube GAS FLOW RATE 1.5 L/Min.

(c) STIRRING SPEED 250 RPM

(d) GLASS WOOL COLUMN

AFTER	474.54 g
BEFORE	474.42 g
TAR	0.12 g

(e) ADSORPTION COL.

AFTER	315.06 g
BEFORE	314.42 g
WATER	0.64 g

(f) FEEDER WEIGHT

BEFORE	1466.97 g
AFTER	1433.25 g
FEED	33.72 g

(g) CYCLONE

AFTER	637.57 g
BEFORE	636.40 g
CHAR	1.17 g

(h) FILTER PAPER

AFTER	2.12 g
BEFORE	1.66 g
CHAR	0.46 g

(i) REACTOR + CYCLONE

AFTER	2190.42 g
BEFORE	2188.57 g
CHAR	1.85 g

(j) OIL VIAL

	I	II
AFTER	25.62 g	14.98 g
BEFORE	14.30 g	14.22 g
OIL	11.32 g	CHAR 0.76 g

(k) GAS METER

AFTER	2550.12 ft³
BEFORE	2544.78 ft³
VOLUME	5.34 ft³

(l) REACTOR (BOTTOM)

BEFORE	940.96 g
AFTER	940.94 g
CHAR	0.02 g

(m) AD. COL. N2 PURGING

AFTER	314.49 g
BEFORE	314.42 g
WATER	0.07 g

(2) REDUCTION OF CATALYST

TEMPERATURE 550 °C

TIME 40 min.

COMMENTS catalyst was reduced earlier (for another run) ~~ie~~, so water production during reduction is very low. No problem during the experiment.

(2) DURING RUN

(a) TIME OF SWITCH TO MAIN 0 Min.

(b) TIME OF RUN 29.0 Min.

(c) TEMPERATURE WITH TIME

TIME, Min.	TEMP., °C	TIME, Min.	TEMP. °C
1.0	560	18	560
2.0	565	21	560
3.0	562	24	559
5.0	562	27	552
7.0	564		
9.0	561		
12	556		
15	552		

AVERAGE REACTOR TEMPERATURE 560 ° C

(3) AFTER RUN

(a) WATER DETERMINATION FACTOR 4.92 mg WATER/ml

(i) WATER IN WASH OIL

DROPER	I	II	III	IV	
BEFORE	1.9011 g	1.7197 g	2.1576 g	1.4901 g	
AFTER	1.5482 g	1.5198 g	1.9109 g	1.1307 g	TOTAL
WASH OIL	0.3529 g	0.1999 g	0.2437 g	0.3594 g	0.956 g
TITRANT	1.32 ml	0.725 ml	0.93 ml	1.33 ml	3.59 ml
WATER %	1.85	1.78	1.88	1.82	1.848%

(ii) WATER IN METHANOL

BEFORE	1.9703 g	3.1479 g	3.5017 g	3.8833 g	
AFTER	1.1349 g	1.1525 g	1.1179 g	1.1341 g	TOTAL
METHANOL	0.8354 g	2.0154 g	2.3838 g	2.7492 g	6.8984 g
TITRANT	0.045 ml	0.14 ml	0.18 ml	0.19 ml	0.51 ml
WATER %	0.026	0.037	0.037	0.037	0.036

(iii) WATER IN VIAL

BEFORE	1.2385 g	1.1172 g	1.2068 g	1.2111 g	
AFTER	1.2013 g	1.0841 g	1.1666 g	1.1734 g	TOTAL
TAR	0.0372 ml	0.0331 ml	0.0402 ml	0.0377 ml	0.1511 ml
TITRANT	7.56 ml	6.715 ml	7.98 ml	7.45 ml	29.99 ml
WATER %	9998	95.35	97.66	97.22	98.27

(b) GAS SAMPLE ANALYSIS

COMPONENT	CALIBRATION GAS			SAMPLE GAS	
	RET.MIN.	VOLUME %	AREA	AREA	VOLUME %
CO	3.90	1.50	0.4315	0.2055	0.7925
CO2	1.26	1.48	0.6395	0.2535	0.5867
CH4	0.55	1.39	1.0639	11.0425	14.4272
C2H4	2.16	0.287	0.4444	0.0	0.00
C2H6	3.08	0.147	0.2355	0.0	0.00
C3	10.48	0.146	0.3640	0.0	0.00
C4+	15.36	0.152	0.4560	0.0	0.00
TOTAL					16.0064

CALIBRATION FOR H2O IN GAS 5.71 ug = 0.25735 AREA

AREA OF WATER PEAK IN GAS = 0.2078

(c) WEIGHT OF WATER

FLASK EMPTY 113.28 g

FLASK FULL 241.36 g

AFTER EVAPORATION 113.38 g

OTHER COMMENTS _____

_____

_____

_____

Mahesh K. Garg 28.02.1985 G-13

INITIAL reactor temperature	530°C	Catalyst Weight	47.40 g
AVERAGE reactor temperature	560°C	Catalyst Type	17.0 % Ni
RESIDENCE time	0.44 s	Catalyst Size	-590+250 um
FLUIDIZING gas rate	4.00 L/min	Total Wood Fed	33.72 g
TOP FEEDER gas rate	0.20 L/min	Moisture content	4.32 %
FEEDER TUBE gas rate	1.50 L/min	Wood Particle Size	-250+105 um
STIRRING SPEED	250 RPM		

TOTAL gas volume 151.21 L

COMPONENT	% Volume (G.C.)	% Volume H_2 free	Weight (g)	%Weight of feed	%Weight of carbon	%Weight of oxygen	%Weight of H
CO	0.9925	6.200	1.717	5.322	4.704	6.879	
CO2	0.5867	3.665	1.613	4.999	2.812	8.224	
CH4	14.4272	90.134	14.446	44.776	69.249		183.205
C2H4	0.0000	0.000	0.000	0.000	0.000		0.000
C2H6	0.0000	0.000	0.000	0.000	0.000		0.000
C3	0.0000	0.000	0.000	0.000	0.000		0.000
C4+	0.0000	0.000	0.000	0.000	0.000		0.000
TOTAL GAS	16.0063	100.000	17.776	55.098	76.764	15.103	183.205

TOTAL YIELD OF COMPONENTS, MF

COMPONENT	WEIGHT (g)	%Weight of feed	%Weight of carbon	%Weight of oxygen	%Weight of H
TOTAL CHAR	2.907	9.009	17.830	4.076	7.317
TOTAL WATER	13.432	41.631		83.704	75.142
TOTAL TAR	0.429	1.329	1.507	1.202	1.079
GASES	17.776	55.098	76.764	15.103	183.205
TOTAL YIELD	34.543	107.067	96.101	104.085	266.744

TOTAL RUN LENGTH, min	29.0	MHSV, 1/HR	1.41
FEED/CATALYST	0.68 hr^{-1}	REFORMABLE GASES (% WT. OF FEED)	50.10
VOL. OF CH_4/FFFD m^3/Kg	0.68	REFORMABLE CARBON IN GAS	96 %
HHV GAS/HHV FEED	1.30	SELECTIVITY FOR CH_4	90 %

TOTAL NO. OF GAS MOLES PRODUCED (per 100 g of feed, mf) 3.10

APPENDIX "C"

TITLE: Catalytic Hydrogasification of Wood - Part of the Bioenergy Development Program

CONTRACTOR:
Waterloo Research Institute
University of Waterloo
Waterloo, Ontario N2L 3G1

PRINCIPAL INVESTIGATOR(S): Dr. D.S. Scott (519)885-1211 x2914
Dept. of Chemical Engineering
Univ. of Waterloo, Waterloo, Ont. N2L 3G1

SCIENTIFIC AUTHORITY: Dr. David P.C. Fung
Dept. of Energy, Mines & Resourc
CANMET, ERL
c/o 555 Booth St., Ottawa K1A 0G1

CONTRACT NO.:
DSS file # 24ST.23216-4-6365

DURATION:
Commencement - Jan. 7th, 1985
Delivery Date - Jan. 1st, 1986

COST: $57,114 (one year)

OBJECTIVE(S):

To investigate a novel gasification method for wood by direct hydrogasification.

RESULTS:

At 500°C-550°C and one atmosphere in an H_2 atmosphere, wood can be converted to CH_4 in a fluidized bed containing catalyst with a carbon conversion to CH_4 of 75% and a gasified carbon selectivity of 95%. It is suggested that a two stage process occurs in a single reactor - thermal pyrolysis followed by methanation. Effect of temperature, type of catalyst, feed to catalyst ratio was investigated. An integrated gasification scheme is proposed.

CONCLUSION:

Wood can be gasified to yield a CH_4-rich gas, or a synthesis gas with CO/H_2 of one, or a H_2-rich gas by suitably designed processes. The process requires input of only wood and a little water. Based on cellulose as a model the overall process is $C_6H_{10}O_5 + H_2O = 6\ CO + 6\ H_2$

RECOMMENDATIONS/

COMMENTS:

Further study at pressures above atmospheric of the hydrogasification step. Test of an integrated system and catalyst life-times.